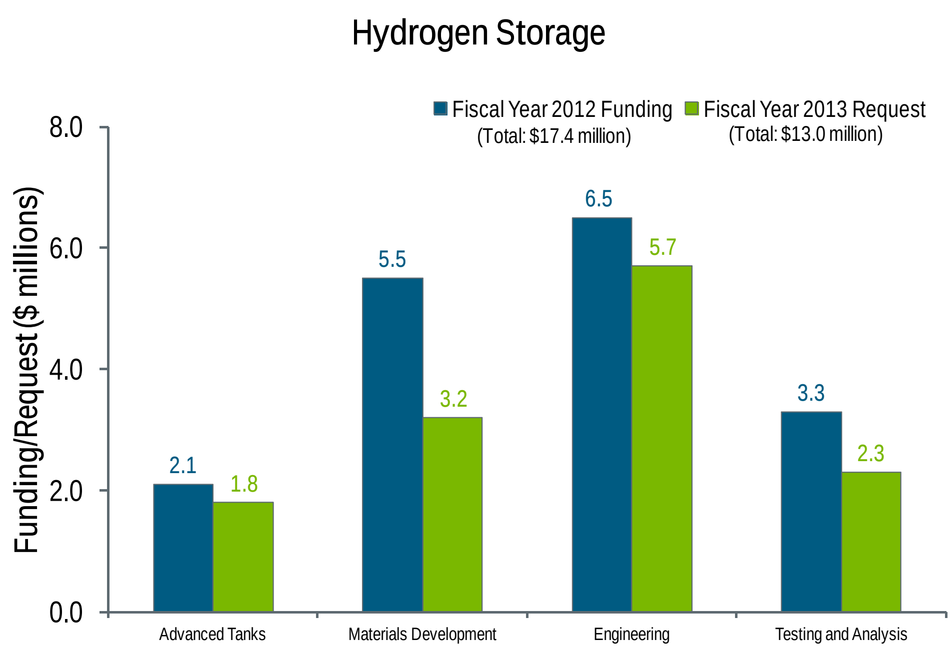
2012 — Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Sub-Program

Summary of Reviewer Comments on the Hydrogen Storage Sub-Program:

The Hydrogen Storage sub-program portfolio was focused in fiscal year (FY) 2012 on system engineering for onboard transportation applications with continued effort in ongoing materials-based research and development (R&D) and physical storage options for near-term applications. Reviewers felt the sub-program was focused and very well managed with good progress shown in the Hydrogen Storage Engineering Center of Excellence (HSECoE). They also supported the sub-program's efforts in expanding into early market applications. Reviewers thought the sub-program was underfunded, making it difficult to support materials-based hydrogen storage to the level needed. Overall, reviewers commented that the sub-program is well managed and organized to focus efforts on achieving U.S. Department of Energy (DOE) goals, and it should continue to review materials and adjust the sub-program's priorities and funding to realize this aim.

Hydrogen Storage Funding by Technology:

The chart below illustrates the appropriated funding planned in FY 2012 and the FY 2013 request for each major activity. In FY 2012, the sub-program received $17.4 million in funding, with a budget request of $13 million for FY 2013. The HSECoE continues to be a major activity for the sub-program. Work directed at lowering the cost of compressed gas storage for near-term commercialization is also a priority along with continued development of materials-based hydrogen storage. In some cases (such as materials development), the funding reduction reflects the completion of prior year projects, with little or no new projects planned in the area in the FY 2013 request.



Majority of Reviewer Comments and Recommendations:

The Hydrogen Storage portfolio was represented by 29 oral and 11 poster presentations in FY 2012. A total of 25 projects (all oral presentations) were reviewed. In general, the reviewers' scores for the storage projects were good, with scores of 3.5, 3.0, and 2.0 for the highest, average, and lowest scores, respectively.

Advanced Tanks: Three projects on advanced tanks were reviewed, with an average score of 2.9. Overall, reviewers thought the work being done was very relevant and good progress was being made. Reviewers approved of the focus on lower-cost precursor materials and the melt-spun approach as key techniques to reduce carbon fiber costs. Reviewers thought the projects had strong collaborations but expressed some concerns with the speed of progress and suggested development of clear risk mitigation plans for each project.

Materials Development: Ten materials-based hydrogen storage projects were reviewed with a high score of 3.4, a low of 2.0, and an average of 2.8. In general, reviewers found the work on materials-based storage options, including investigations of metal hydrides, chemical hydrogen storage materials, sorbents, and liquid carriers, highly relevant to sub-program goals. Reviewers commented on the strong collaboration evident in many projects and noted the robust theoretical and computational efforts in explaining and guiding progress in materials development, particularly work on metal organic frameworks (MOFs). However, many reviewers felt experimental efforts could be more focused to provide stronger evidence in support of the theoretical work. Materials projects will continue in FY 2013, subject to appropriations, with an emphasis on a stronger link and feedback route between the experimental and theoretical efforts.

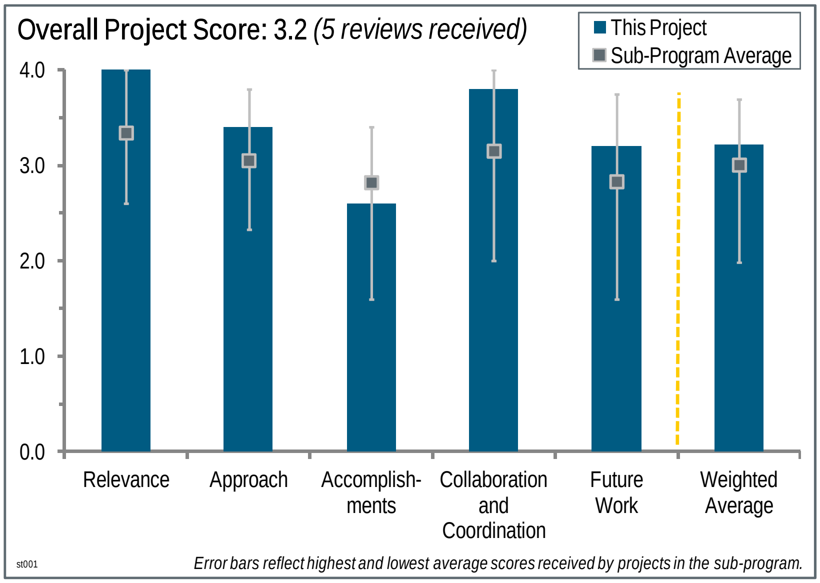
Engineering: Eleven projects were reviewed on hydrogen storage engineering, with a high score of 3.5, a low score of 2.9, and an average score of 3.3. Overall, reviewers believed the HSECoE made significant progress in FY 2012 with strong coordination and clear collaboration among the 10 partners. They also remarked on the difficulty in engineering complete systems without a material that currently meets all system requirements, but noted the importance of systems engineering occurring in parallel to materials development to help achieve the Hydrogen and Fuel Cells Program’s goals. Substantial effort on chemical hydrogen and sorbent storage systems as well as physical storage tasks was regarded favorably by reviewers along with the development of key models. In general, for the individual partner reviews, the projects were thought to be well thought out with expert personnel to execute clear plans. Reviewers expressed concern about overlap between certain projects and a focus on ammonia borane at the expense of alane for chemical hydrogen storage systems. Reviewers believed work on elements not unique to specific materials was particularly beneficial, including engineering modeling of balance of plant issues, failure mode and effects analysis, and the systems analysis of hydrogen storage impacts on the global vehicular system. In general, it was thought the HSECoE and its partners were making good progress in evaluating materials-based storage systems and making decisions to meet DOE performance targets.

Testing and Analysis: One project related to testing and analysis was reviewed, with an overall score of 3.2. Reviewers felt this area was critical to the sub-program, as it provided important information and guidance for achieving DOE goals and successful program management. Reviewers believed this project made good progress in updating analysis of physical storage systems, para-ortho conversion of hydrogen in cryocompressed and MOF-5 adsorption systems, and completing onboard analyses for ammonia borane/ionic liquid and alane slurry chemical storage systems. However, they felt this effort would benefit from more industrial partners and that additional validation of model assumptions would be good. Overall, reviewers believed this work utilizes a strong team of analysts and consistent methodology to develop comprehensive analytical tools beneficial to the sub-program.

Project # ST-001: System Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:
The objectives of this project are to: (1) conduct independent systems analyses for the U.S. Department of Energy (DOE) to gauge the performance of hydrogen (H_2) storage systems; (2) provide results to material developers for assessment against performance targets and goals and to help them focus on areas requiring improvements; (3) provide inputs for independent analysis of onboard system costs; (4) identify interface issues and opportunities, as well as data needs for technology development; and (5) perform reverse engineering to define material properties needed to meet the system-level targets.



Question 1: Relevance to overall DOE objectives

This project was rated **4.0** for its relevance to DOE objectives.

- Accurate analysis is critical to guide the storage program and to ensure that storage options are reasonable at a systems level.
- This is a key project in terms of enabling meaningful cost estimates. This is a very important goal and is required for proper program management.
- Argonne National Laboratory (ANL) is providing in-depth and high-quality systems analyses that support the Hydrogen Storage sub-program with respect to the assessment of various storage approaches compared to performance targets for light-duty vehicles. ANL's results provide important insights on the attributes and limitations of current configurations toward meeting technical and cost goals. This information has been very useful for making go/no-go decisions on the continuation of several storage development projects as well as providing independent insight on the progress and potential of storage systems.
- This project provides comprehensive and quantitative systems analyses of H_2 storage approaches. The project is a solid complement to the work being conducted in the Hydrogen Storage Engineering Center of Excellence (HSECoE), and the technology assessments performed in this project provide DOE with an independent, objective evaluation of storage system options. The project fully supports the DOE research, development, and demonstration (RD&D) objectives.
- The H_2 storage system analysis is highly relevant to the DOE RD&D objectives because this type of effort provides a clear status assessment of the various storage systems to compare to the DOE targets. The project area that is not as relevant is the 70 MPa fast-filling analysis. This research is not aligned with the codes and standards effort that is occurring with the Society of Automotive Engineers (SAE) Standard for Fueling Protocols for Light Duty Gaseous Hydrogen Surface Vehicles, SAE J2601, and it is not consistent with the project scope, which should be focused on storage system analysis.

Question 2: Approach to performing the work

This project was rated **3.4** for its approach.

- ANL has assembled a talented team with capabilities in several modeling areas to address relevant issues in the storage program.

- The principal investigator (PI) consistently has an effective approach to his system analysis. It could be improved based on additional steps to validate the models. In particular, the tank composite winding and fast filling should be confirmed based on data. Other system development models could benefit from a confirmation in the assumptions based on data or a reference to gain confidence in the transfer functions used within the models.
- The methods for carbon fiber (CF) tank work are good and appropriate. The tools are getting to be the right ones. It is not clear that the para-hydrogen to ortho-hydrogen work adds much to what Lawrence Livermore National Laboratory (LLNL) has already done. However, adding the para-to-ortho (PO) energy is a valuable addition to the existing model for cryo-compressed storage.
- The ANL approach generally considers essentially all of the relevant technical parameters needed to assess the ability of a given storage system to meet both the onboard and off-board performance targets. ANL collects and updates inputs from various sources to obtain reasonably complete descriptions of H_2 storage systems, and the laboratory's analysis methodology seems to be thorough and sound. The major limitation is the lack of sufficient details on specific properties of incompletely characterized systems (e.g., reliable reaction rates for H_2 reaction with the storage media in the appropriate operating temperatures, or important parameters such as thermal conductance of powders or compacted sorbents). ANL has exchanged information with several partners of the HSECoE. The consistent application of trade studies to determine the influence of various parameters is also valuable to identify which parameters have the most impact on achieving or limiting the performance targets.
- A solid technical approach focusing on the use of thermodynamic and kinetic models and trade-off analyses to evaluate different storage systems has been adopted. The major effort on this project in 2011 and 2012 addressed issues in two areas: (1) cost reduction and efficiency improvement in compressed gas storage systems utilizing CF-wound tanks, and (2) increased capacity in cryogenic systems employing metal-organic framework-5 (MOF-5) as a storage medium. Additional work included analyses devoted to optimization of conditions for H_2 discharge from a carbon, boron, and nitrogen (CBN) material, and a new process for improving the efficiency of ammonia borane (AB) regeneration. Although the approaches that were used to explore these different system options were well formulated, the priorities are somewhat concerning. First, there has been a tremendous amount of work conducted by tank manufacturers and other research centers on the reduction of CF usage without compromise of tank strength. Although the proprietary nature of some of that work is acknowledged, it is not totally apparent that the ANL project has provided any new or particularly useful information about CF tank improvements. Likewise, significant efforts are underway at the HSECoE and elsewhere on the use of cryo-confinement using MOF-5. There should be a more robust link between the ANL project and other DOE-sponsored efforts in this area. The efficient, off-board regeneration of AB and the elimination of contaminants (e.g., borazine, diborane, and ammonia) during onboard H_2 release from AB are critical issues that have not received enough attention. Although the analysis of a benzophenone-based process for AB regeneration was compelling, the overarching problem of hydrazine cost remains. Likewise, the issue of contaminant elimination in an onboard AB system is still problematic. Moreover, there is almost no work being conducted on the equally important problem of alane regeneration. Instead of focusing on problems that are already being thoroughly addressed (e.g., CF tanks and cryo-storage improvements), the impact of this project would be greater if the focus was on problems that are not already being explored extensively in other projects.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.6** for its accomplishments and progress.

- ANL efforts during the past year were in updating assessments of physical storage systems—mainly compressed gas, assessments of P-O conversion of H_2 on cryo-compressed systems and on MOF-5 adsorption systems, and completing onboard analyses for AB/ionic liquid (IL) and alane slurry chemical storage systems. ANL's analyses indicate that serious limitations remain with all of the materials-based approaches for H_2 storage. ANL's assessments on the off-board performance of AB/IL point out that severe issues remain with the hydrazine regeneration of AB on the wheel-to-tank efficiencies below 20%. Once again the ANL team has investigated a broad range of systems in considerable depth, resulting in two valuable publications in the literature.
- Incorporation of P-O H_2 conversion is a good addition and a significant result. The AB regeneration work is a very important contribution. The project team should consider looking at economic analysis as well.
- In comparison to last year, the progress was not evident for the funding amount. Also, ANL was previously funded to assist in providing composite tank estimates for the cost estimating performed by TIAX. It appears that this work is being repeated for the new Strategic Analysis, Inc. (SA), (formerly Directed Technologies, Inc.)

work. In previous years, this project always provided a summary of the current H_2 storage technology that has been analyzed and updated. This year, the project review did not include any summary or reflection of any progress in the storage system attributes.
- The key function of compressed tank models came up unusually low in material used, which is a problem. The O-P conversion impacts are a useful addition to the model structure, though of course LLNL has already pointed out much of the results. However, it was useful to include this in the ANL model. Efficiency of AB processes is useful, though it may be that the project team feels that the very low levels of efficiency stated are acceptable, and this is absolutely not right.
- Good progress was made in all areas. However, a concern that was expressed in the 2011 review remains: only very limited information is provided concerning the remaining areas of risk as well as challenges that must be addressed for the systems that were investigated. Likewise, a detailed risk mitigation strategy is not evident. In addition, a discussion of related work that is being conducted in other laboratories would be useful in order to place the ANL work in the proper context. For example, the ANL results on CF tanks, MOF-5 cryo-systems, and AB regeneration should be compared and contrasted with those obtained in related efforts at other laboratories.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- In general, fruitful collaborations with other organizations are evident. The overall impact of the project has been enhanced by those interactions; however, a closer collaboration with the HSECoE, especially on the cryo-compressed H_2 systems, is needed. The project is well managed, and the systems analyses are being conducted by a first-rate development and engineering team.
- ANL has identified a good set of partners to collaborate in its work. There is good collaboration with SA, PIs, and others.
- The collaboration is with the right people and is especially effective. This is not a list of people the project team talked to, but rather groups it has materially helped.
- ANL worked with TIAX in predicting both onboard and off-board costs for several storage systems and with SA on compressed gas systems. There were close interactions and an exchange of technical information with a number of other organizations within the HSECoE, which has been a benefit to the Hydrogen Storage sub-program. ANL also worked with the University of Oregon on regeneration reactions for the chemical storage system CBN.
- The collaboration with the industry is good, and ANL is active in various forums to provide information. It would still be useful to be engaged with the HSECoE project. In particular, the exchange of balance-of-plant assumptions would be highly recommended, as would a further comparison of approaches.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The proposed future work seems consistent with what the project team is charged with doing. The calibration of the tank model is a very, very good plan to calibrate models to known systems.
- It would be nice if ANL could look at alane regeneration.
- The future work outline appears fine except for the effort on the 70 MPa filling analysis. Also, additional proposals for tank optimization (i.e., end caps) need to be coordinated with a tank manufacturer and/or manufacturing trials.
- The future work is a straightforward extension of the 2011 effort. However, there is an overemphasis on physical storage, especially CF tank improvements. Those improvements are being addressed in detail elsewhere. The remaining resources should be directed to problems associated with AB and alane regeneration, contaminant reduction during H_2 release from AB, and improved CBN regeneration chemistries.
- There should be further comprehensive analyses of the compressed and cryo-compressed storage vessels that include variations in design configurations and optimization that address manufacturing constraints for safety and structural materials (e.g., CFs, aluminum versus stainless steel, optimization of designs, and fiber wrapping). ANL should continue, as planned, to assess the properties of promising chemical storage materials such as CBN

and related compounds. Other options also should be considered as information becomes available from new studies just started within the Hydrogen Storage sub-program.

Project strengths:

- ANL has developed very comprehensive analytical tools for detailed engineering assessment of both the onboard and off-board aspects of H_2 storage. ANL's results appear to be very reliable and robust from comparisons that have been based on current knowledge and experience of others with available prototype and demonstration storage systems. The engineering staff at ANL has provided clear presentations of its methods and results. Analyses appear to be based on the best available data from various sources.
- The project has several strengths: a strong team of analysts, good collaboration with academic and industrial partners, and consistent methodologies for analyses.
- One strength is the history of models that allows a consistent comparison across technology.
- This ANL project has consistently been an excellent resource for H_2 storage system analysis. The analytical methodology is typically a strength of this project.
- This project is providing DOE with useful information concerning the design and implementation of an optimum onboard storage/delivery system. The analyses and engineering efforts are being conducted by a strong team with considerable expertise in thermodynamic and kinetic modeling for systems applications.

Project weaknesses:

- DOE should strive to ensure that the analysis effort has the resources it needs to carry out relevant analyses.
- This project would really benefit from multiple industrial partners or coaches at least; DOE and its technology team are not enough. There is not enough contact with them to drive good realism into the code.
- A straightforward discussion of the present work in the context of previous studies is lacking. Likewise, a candid risk analysis and robust mitigation strategy for each of the candidate systems is missing.
- As was also noted in last year's review, the primary challenge for these analyses by ANL is the limited availability of reliable and complete reaction parameters (i.e., kinetics data) for the various H_2 storage media over sufficiently broad temperature ranges to generate robust predictions of performance in specific designs. Without the capability of generating the necessary input parameters, ANL appears to sometimes extrapolate properties outside of reasonable limits and may not be capable of fully establishing the correct behavior.
- As indicated, the project needs to include some level of validation or confirmation of the model assumptions. The composite tank analysis and the proposals for the end cap design need to be reviewed with a manufacturer to confirm the results. The end cap concept needs to have an understanding of how to join the end cap to the tank. The reason for the fast-fill analysis is unclear because 70 MPa Type IV tanks have also shown the need for pre-cooling.

Recommendations for additions/deletions to project scope:

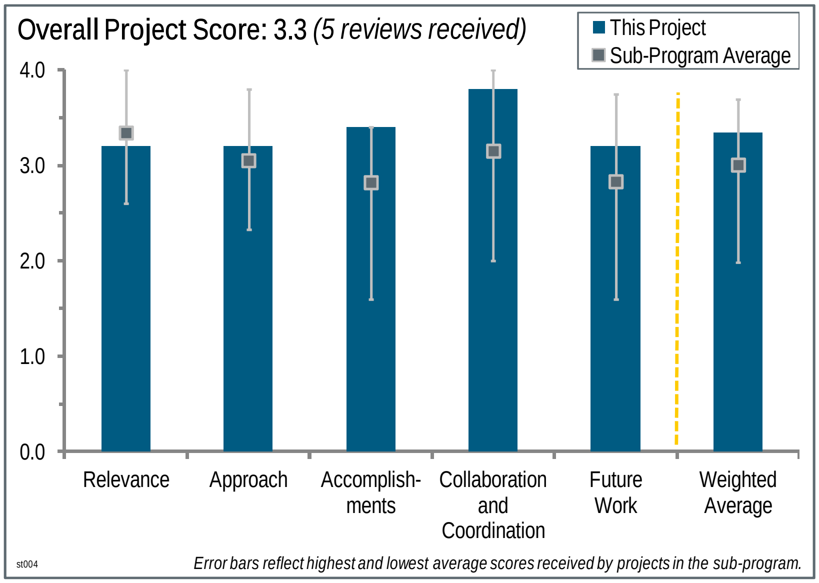
- The team should validate the composite tank analysis, seek proactive engagement with the HSECoE, and provide further validated information about the rates involved with the P-O conversion.
- The project team should delete the effort with improving the liner conductivity for the fast-fill analysis and replace it with analysis to study the increase in temperature limits from 85°C to a higher temperature. The physical storage systems should be de-emphasized in favor of more in-depth and extensive analyses of chemical storage systems. The problems and challenges associated with the latter (especially AB, alane, and CBN regeneration) are significant, and given the importance that is being placed on chemical H_2 storage materials in the DOE portfolio of engineering activities, a focused and innovative effort that addresses those problems is needed.
- ANL should continue to focus on comprehensive assessments of the physical storage systems in configurations that can be used in near-term vehicles and early market applications. Unless an AB regeneration scheme can be identified with greater than 40% efficiencies, there does not seem to be a need for further onboard and off-board assessments of the AB/IL storage system. However, more work on properties and behavior of chemical storage based on CBN materials and similar candidates is acceptable. ANL should look into the regeneration of $LiAlH_4$ via the dimethyl ether process developed by the team of Jensen/McGrady from the Metal Hydride Center of Excellence. Finally, there should be continued collaboration between ANL and the HSECoE to maximize information exchange.

Project # ST-004: Hydrogen Storage Engineering Center of Excellence

Don Anton; Savannah River National Laboratory

Brief Summary of Project:

The objective of this project is to develop materials-based hydrogen (H_2) storage systems for onboard H_2 storage for light-duty vehicles. This includes a three-phased approach of: (1) establishing system requirements and novel concepts (answering "where are we?" and "where can we get to?"); (2) novel concept modeling design and evaluation (answering "how do we get there [close the gaps]?" and "how much further can we go?"); and (3) subscale prototype construction, testing, and evaluation (putting it all together and confirming claims).



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.2** for its relevance to DOE objectives.

- Given the fact that no material exists that comes close to meeting all requirements (including cost), engineering efforts may be premature.
- The project supports the DOE onboard H_2 storage objectives for three categories of technologies out of a larger set of choices. For the three methods the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) is tasked with, it has done a very good job of improving and organizing the understanding of metal hydrides, chemical H_2 storage materials, and adsorbent systems.
- The Center is addressing a well-considered set of "barriers" to the H_2 storage system aspect of the DOE Hydrogen and Fuel Cells Program (the Program). The targets are based on realistic assessments of storage system requirements. The notion about the need to do materials development and system engineering in parallel is absolutely correct at the present stage of the Program. The spider chart approach provides a clearly illustrative means of tracking progress toward meeting targets in a timely manner.
- The HSECoE project is focused on evaluating different candidate storage systems and developing engineering solutions that utilize the material systems whose storage characteristics are most closely aligned with DOE targets. Unfortunately, no single material system that meets all of the DOE targets has been identified. Consequently, the overall technical effort has (by necessity) comprised materials development activities as well as the more relevant systems engineering problems. Overall, the HSECoE work is a vital part of the H_2 research, development, and demonstration program. However, the absence of an ideal storage material has generally limited its impact.
- If there were a material(s) that had the requisite properties to enable a viable storage system to be designed, the HSECoE relevance would be excellent. If surrogate materials are not sufficiently advanced, a viable prototype storage system may not be possible. In that case, the Center's relevance is in question and the resources devoted to the Center would have been better spent in materials discovery. However, it is too soon to know if the Center will proceed into Phase III.

Question 2: Approach to performing the work

This project was rated **3.2** for its approach.

- The Center is doing a good job of understanding the onboard system. Little is being done on off-board systems. This appears to be a program issue not under control of the Center. The Center is doing a great job of using project management tools to manage its program and ensure that tasks are on target and on time.
- The overall approach would indeed be difficult to improve upon. The HSECoE is presently in the middle of Phase II and the approach appears to be working well. A major emphasis in terms of storage medium development is focused on adsorbents and liquid-phase chemical storage materials. Work on other materials options was discontinued for well-determined reasons. Go/no-go logics are being applied in a timely and definitive manner. A sensible plan is emerging in the approach wherein the Center will go forward with the best overall storage medium, where "best" is determined by how well the storage medium can collectively meet targets regardless of whether or not all of the targets can be met. It is probably going to turn out that by the end of Phase III, the final "best" H_2 storage system will still fall short in terms of meeting "system" gravimetric and/or volumetric storage targets, but that does not mean the system could not be applied in numerous present-day transportation infrastructures.
- The HSECoE has adopted an two-pronged approach focused on: (1) the evaluation of storage materials candidates and selection of the best material systems for incorporation into an engineering test system; and (2) design, implementation, and validation of innovative system architectures that employ those materials. The current materials limitations notwithstanding, this is a sound and compelling strategy, and the HSECoE has done a good job of identifying key technical barriers and developing engineering strategies that address those challenges.
- While an ideal material does not exist, the Center's approach is to use a combination of modeling and simulation and characterization of surrogate materials to address the engineering issues and challenges that must be overcome to design a prototype storage system. This combination of modeling and subcomponent and material characterization is sound. However, what is not clear is how close to the DOE targets a surrogate material needs to be to enable a viable storage system to be designed and built. The decision process to proceed into Phase III and build a system needs clarification and some additional DOE input. The management structure is sound and the matrix approach appears to be working well. Communication among the team members appears to be very open and cooperative.
- Given the limited materials and physical processes available, this project has done a good job charting a course to identify H_2 storage possibilities that also have the constraint of meeting the needs of light-duty vehicles and reasonable fuel infrastructure. This has been a long program with a reasonably good engineering approach. However, at about $6 million/year, it would be important to recognize when a no-go or down-select is appropriate, and act at that time, even if it is earlier than the planned go/no-go date. In that context, it would be interesting to know if work was performed on metal hydrides and dry, solid-phase chemical H_2 storage materials even though the no-go was known.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.4** for its accomplishments and progress.

- The year-over-year progress toward DOE performance goals for systems and processes for adsorbents and chemical H_2 storage materials has trended well. The engineering accomplishments were the primary reasons for this.
- The Center has done a good job on its $NaAlH_4$ system to understand performance optimization and trade-offs. The photos of the alanate pellet are frightening because they show significant degradation of the pellet. Adsorbent work to understand thermal and permeability issues is a significant accomplishment.
- Significant progress has been made toward meeting objectives and overcoming one or more barriers. The exploration and assessment of metal hydride storage materials was comprehensive and to the point. The rationale for ending work on metal hydrides was clearly presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR). The stepwise projection of plausible improvements that will allow 2017 gravimetric H_2 storage targets to be met for chemical H_2 storage materials is well thought out, but it is also very ambitious and seems (more than anything else) to depend on being able to increase the ammonia borane (AB) loading. The

baseline values for system gravimetric and volumetric H_2 storage for the adsorbent approach still fall significantly short of meeting 2017 DOE targets. Also, plausible progress steps that are proposed to bring both of these parameters into line with the targets are somewhat conflicted. The failure modes and effects analysis activity fits well into the work of the HSECoE at this time. It is somewhat concerning that the outcome of these studies may turn out to adversely impact the Center's ability to meet/sustain established performance targets.

- A careful and well-formulated effort has been conducted to down-select two classes of storage systems; namely liquid-phase chemical H_2 storage materials and adsorbent-based systems ("spider charts" provide a useful snapshot of material status relative to DOE goals). This has allowed the HSECoE to more effectively direct the technical effort and resources in future work. In addition, identification of important technical barriers has been provided. That said, there are three general concerns: (1) Based largely on the excellent work conducted in the Chemical Hydrogen Storage Center of Excellence, AB has been selected as a candidate for further development in the HSECoE. Although "H_2 purity" is mentioned as a technical challenge, the use of multiple scrubbers to remove those compounds seems unwieldy and cumbersome, and implementation in a complete system seems problematic. A more innovative solution is needed. (2) AlH_3 remains a solid contender for development in an engineered system. However, the Center is so strongly focused on the AB system that alane is becoming marginalized. Moreover, it seems unlikely that the engineering solutions that apply to the exothermic AB system will be appropriate to an endothermic release material such as AlH_3. (3) Given the rapid pace of adsorbent material development, other candidates (besides metal-organic framework-5 [MOF-5]) should be carefully considered and evaluated for the cryo-adsorbent system application—hopefully that will be done in the system architecture work next year.
- The accomplishments in 2011 have been very good. Down-selection was completed for the reversible metal hydrides and characterization data for AB, and the activated carbon sorbent AX 21 was obtained, which allowed critical issues to be identified and subsystem designs to be developed. Potential improvements for each system have been identified and their impact on system characteristics has been projected. If all of the improvements are realized, the AB system appears able to meet the onboard 2017 system targets. Some compromises in gravimetric density of adsorbents need to be made to meet the volumetric density and cost. In addition, failure modes and effects analyses for both systems were completed. Preliminary cost estimates for each system have been developed, but it is not possible to assess whether the costs will meet the DOE targets because they have not been finalized by DOE and the U.S. DRIVE Partnership partners.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- The Center appears to continue to do a very good job in coordinating the program and the member institutions.
- The Center has assembled a good team to carry out its work and appears to be taking a very proactive approach in promoting active engagement and collaboration among its members.
- Coordination across the Center is first rate. Individuals and organizations that are assigned various aspects of the effort report their progress to their respective system architect, who is responsible for all of the development activities along a given pathway. Information flow from the previous three materials centers is facilitated by individuals transitioning from those centers to the HSECoE team.
- The collaborations with partnering institutions are very well coordinated by the HSECoE; the evidence for this appeared seamlessly throughout the presentation by Don Anton (as it should be in an effectively orchestrated multi-partner project). Indeed, Savannah River National Laboratory (SRNL) has accomplished this level of partner interconnection through careful selection of collaborating institutions and personnel, regular progress meetings, and common databases.
- A solid management plan is in place and good communication channels seem to be in place among the many partners in the Center. However, given such a large and complex entity, a fully engaged coordinating council or executive committee is of vital importance to assist the director in assessing progress, coordinating activities, and suggesting possible "mid-course corrections" and redirections of technical work that will undoubtedly occur. The role of a coordinating council is missing from the "management" section of the presentation.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The future plans are focused on well-considered key "steps" that have been identified (and are being intensely investigated) for boosting all underperforming system parameters to the 2017 DOE system target values.
- The future work on the chemical H_2 storage material and cryo-adsorbent systems is given in sufficient detail to provide confidence that a well-focused technical effort will occur in those areas. Reasonable milestones are in place, and a technical plan consistent with meeting those milestones has been formulated. A more extensive effort on developing an alane-based engineering subsystem would be desirable.
- Given the low efficiency and high cost of AB regeneration, the Center should not work on chemical H_2 storage material issues unique to AB, such as ammonia removal. Its focus should be on issues common to any off-board regenerable materials.
- The future work plans are good and address the unresolved component design and performance issues and challenges leading up to the Phase III decision point. The Center has made projections for future improvements in materials and component characteristics that indicate a pathway to meeting the DOE targets for the adsorbent and chemical H_2 storage material systems. It would be helpful to understand the likelihood of each of these steps achieving the desired improvements, for example, the likelihood that the thermal conductivity of MOF-5 will be increased by an order of magnitude.
- Regarding the proposed future work on chemical H_2 storage materials and adsorbent work on slide 38, it is unclear if there is enough time in the 11 months left before the go/no-go decision. The presenter did mention the possibility of a no-cost extension, and at 55% complete on 3/31/12, it could easily be necessary. There may be challenges in trying to increase the AB concentration in the slurry from 65% to 85%. There are a number of time-consuming variables to consider in understanding the implications of liquid and powder properties on slurry rheology.

Project strengths:

- This project features excellent management, effective collaborations, a well-orchestrated approach, a properly focused emphasis on the research and development tasks, and an overall plan that promises to be a success story at some level.
- The Center has assembled a great team. Center management has been very proactive in managing the team and keeping it focused on tasks and overall goals.
- The project has an excellent team and management structure that takes full advantage of the experience gained in the earlier materials centers. It also features excellent collaborators. The project made good response to comments from last year's review comments.
- The main strength is the aggregate set of capabilities of all of the partners. The general approach in meeting the objectives has probably helped keep focus on a project with a wide range of diverse tasks and technologies to meet a common goal.
- The HSECoE comprises a well-qualified team with strong backgrounds and expertise in material assessment, engineering modeling, and prototype development. A solid technical approach has been adopted, and there has been good progress on meeting the overall goals of the project. Specifically, the Center should be recognized for conducting a careful and objective evaluation of multiple material candidates and making the go/no-go decisions that were needed to provide a better focus for development of system solutions in the future.

Project weaknesses:

- There really are not any weaknesses, as far as the SRNL component of the HSECoE is concerned.
- The overarching problem that faces the activities in the Center is that no single material that meets the DOE targets has been identified. This has forced the Center to concentrate on a variety of less-than-ideal systems. Hopefully, the information gained from that work will translate effectively to a more capable material system that may emerge in the future.
- The Center focuses on the storage system and performance onboard. Very little is being done on off-board regeneration. The entire system needs to be optimized rather than just the onboard system. As stated earlier, this is an issue for the Program—it is not under the Center's control.

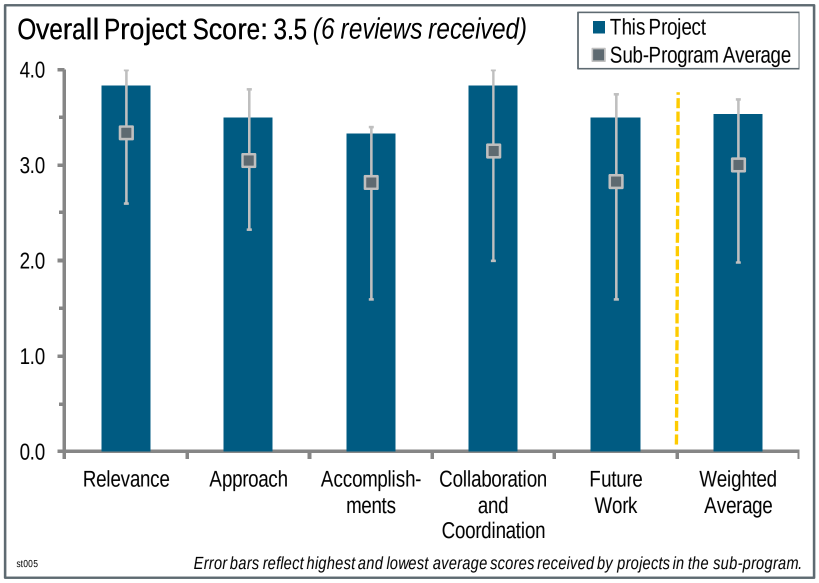
- One weakness is the lack of a suitable material that would enable a truly viable materials-based storage system. This is not necessarily the Center’s fault, but it could lead to a diminution of the Center’s accomplishments.

Recommendations for additions/deletions to project scope:

- There should be more collaboration with analysis efforts to include forecourt issues.
- In next year’s AMR presentation, the project team should consider an overlay approach to the spider charts that should project the year-to-year progress made by the HSECoE. This reviewer has been assured by Don Anton that the modeling activities being performed across the HSECoE are all appropriately integrated and use the same framework, basis, etc. At the 2013 AMR it would be a good idea to illustrate to the audience how this integration is accomplished.
- A more robust effort on the design and development of an alane-based subsystem is recommended. The present work focuses strongly on AB. It is unlikely that the engineering trade-offs identified for that material will apply equally well to alane. The Center management and coordinating council should take precautions to avoid unnecessary overlap of activities in this large and complex center. Special attention should be paid to limiting the duplication of system modeling efforts in the National Renewable Energy Laboratory (project ST-008) and Ford/BASF-DE/UM (project ST-010) projects. Finally, it is known that work on developing a strategy and engineering solution to off-board regeneration is outside the scope of the Center activities. However, the cost and efficiency of the regeneration process(es) remain daunting and critical challenges. The DOE Office of Energy Efficiency and Renewable Energy should consider a parallel activity to more fully explore system solutions to the spent fuel regeneration problem.
- Consider a “reality check” modeling step that uses the bill of materials’ output from the HSECoE system engineering and couples that to the system’s capital and fuel cost model. Such a step may illuminate bad cost trends early and save some time. The AB slurry is still subject to AB’s thermal stability at temperatures in the 50°C to 80°C range. For a fuel transported and stored in an infrastructure or on tanker trucks that can be in locations where the air is 50°C–55°C, it would be worthwhile to look into this. It would be easy to do a time-temperature-decomposition study in an environmental chamber, or in Palm Springs in the summer.

Project # ST-005: Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

Jamie Holladay; Pacific Northwest National Laboratory



Brief Summary of Project:

The overall objectives of this project are to: (1) design chemical hydrogen (H_2) storage system and balance-of-plant (BOP) components; (2) develop system models to predict mass, volume, and performance; (3) reduce system volume and mass while optimizing storage capability, fueling, and H_2 supply performance; (4) mitigate materials incompatibility issues associated with H_2 embrittlement, corrosion, and permeability; (5) demonstrate the performance of economical, compact, lightweight vessels for hybridized storage; (6) guide design and technology down-selection via cost modeling and manufacturing analysis; and (7) perform value engineering of BOP to minimize cost, volume, and mass.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.8** for its relevance to DOE objectives.

- Both the tank analyses and the chemical H_2 storage work are highly relevant.
- There are few current technical options for vehicular H_2 storage, and the options in this project represent a major hope for providing an H_2 storage solution for this key application—light-duty transportation.
- This project is relevant to DOE's objectives for the development of viable onboard physical and chemical H_2 storage systems. Pacific Northwest National Laboratory (PNNL) provides analysis and data in support of the Hydrogen Storage Engineering Center of Excellence's (HSECoE's, the Center's) go/no-go decision on chemical H_2 storage options.
- The HSECoE's value is good, but it would be outstanding if researchers were closer to materials that had the potential to meet DOE targets. Cost and production efficiency of ammonia borane (AB) will likely preclude its use as a storage material. Vessel optimization is appropriate because it spans all technologies. Engineering modeling of BOP issues is important.
- This project is a centerpiece of the overall HSECoE. In this project, the key deficiencies in chemical H_2 storage material properties are addressed, with an emphasis on mitigating those deficiencies up to the point of meeting or surpassing 2017 DOE H_2 storage system performance targets. This is done through a process of materials property enhancement and the development of novel engineering solutions. As such, this project contributes key materials performance and system architecture information needed for full system analysis. In addition, the project develops and transmits modeling/simulation tools, prototype systems, engineering methodologies, and similar tools to the greater H_2 storage community.
- It is very important to demonstrate commercially viable H_2 storage systems other than cryo tanks. It is a mistake that there is not ongoing material development working in parallel with the HSECoE. The impact of system operation and packaging on the chemistry of the fuels is not possible to predict a priori, and engineers do not have sufficient molecular level expertise to "engineer" solutions to these "material deficiencies." A cynic might suggest that perhaps the engineers could consider engineering to accommodate a material's set of properties instead, but it is more appropriate to just be practical and recognize that the DOE goals are very challenging and cannot be expected to be achieved without a multifunctional team that includes a widely diverse set of technical

backgrounds and synthetic and physical chemists along with the engineers. The PNNL team appears to have the balance necessary to achieve DOE's goals.

Question 2: Approach to performing the work

This project was rated **3.5** for its approach.

- Finite element analysis on wall thickness is appropriate and well-designed and well-executed. Materials screening for Type IV tanks is appropriate and done well.
- PNNL provides strong support of HSECoE activities in chemical H_2 storage, pressure vessel, and BOP. The project utilizes both modeling and experiment efforts to address DOE targets in weight, volume, cost, durability, and efficiency. There is a lack of information on BOP components (heat exchanger, pumps, valves) that could work with PNNL's AB slurry fuel system.
- The comparison of exothermic AB and endothermic alane slurry approaches is very good. The slurry AB approach is interesting, but identification of the best liquid for the slurry approach is the key. Also, slurry instability (settling out of the reacted AB) is an important issue. It is unclear if the slurry approach has been compared to the AB ionic liquid approach.
- This project features a very good approach, mixing the pressure vessel and choices for endothermic and exothermic material options with options for slurry and liquid. There is a statement on slide 4 about guiding design and technology down-selection using cost modeling and manufacturing analysis—this also needs performance as a criteria. It may be implied in the slide that discusses combining predictive models with cost models, but that should be in a broader context for this overall project.
- The study of pressure vessels as an enabling technology is a key aspect of this project. The manufacturing and performance issues being addressed are central to the goal of meeting DOE 2017 H_2 storage system cost and performance targets. The approach to chemical H_2 storage system development is focused on reducing system volume and mass to improve the overall performance of the system in terms of deliverable H_2 per system volume, system weight, and system cost. Experimental and modeling studies are appropriately integrated to optimize system performance parameters, mainly in the context of meeting DOE 2017 H_2 storage system targets. A number of other important H_2 storage system issues are also addressed in ways that are generally applicable to all storage material concepts. Information pertinent to go/no-go decision points is being developed in a concerted manner that is well aligned with HSECoE objectives and timelines.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.3** for its accomplishments and progress.

- The incorporation of cost into tank models is a significant step. Vehicle level modeling to predict materials performance is well done.
- It would appear that the slurry alane results are unfavorable compared to the slurry AB results, with regard to the gravimetric storage system characteristics. The project team did nice work on the optimization analyses of the tanks.
- Good progress was made in characterizing AB slurry properties. The settling of spent slurry (within hours) could be problematic for refueling. Cryogenic testing of polymer liner material provides critical data to assess the applicability of Type IV tanks for cryo-adsorbent or cryo-compressed H_2 storage options. It is not clear what fatigue limits are referred to in PNNL's analysis of Type III tanks. It is unclear if they are derived from stress versus the number of cycles to failure curves established by ASME, and whether the finite element analysis accounted for the changing material strain/stress behavior after hundreds or thousands of cycles.
- Significant progress toward meeting HSECoE program objectives and elucidating pathways to eliminating performance barriers has been made in the past year. In the pressure vessel area, there are still uncertainties and limitations that need to be resolved, particularly with respect to demonstrating Type IV vessel performance and meeting cost targets. In the chemical H_2 storage material development area, gravimetric storage density and plant efficiency targets remain to be met. Accomplishments from the liquid slurry work are both impressive and encouraging.
- The study of polymer liner material, dehydration kinetics, and the initial phase of AB slurry properties have been valuable accomplishments; combined with the other accomplishments, they are still small in comparison to the

significance of the accomplishments hoped for from the future work. Overall, most of the leverages of this project seem to rest on the future work.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- This is a well-balanced team of scientists and engineers.
- This project features good work across Center partners and vendors.
- The project seems to be effectively coordinated and used partners' capabilities and contributions.
- PNNL has close interaction and collaboration with members of the HSECoE. More active information exchange with members of the Storage Systems Analysis Working Group is encouraged.
- The collaborative activities that connect to this project are all clearly aligned with specific needs and objectives of the HSECoE in areas that support the tasks and responsibilities assigned to PNNL. Each collaboration addresses a clearly defined need or issue that fits into the pathway for completion of key performance and cost validation milestones.
- It is unclear what the collaboration is with Los Alamos National Laboratory (LANL) on the AB ionic liquid approach.

Question 5: Proposed future work

This project was rated **3.5** for its proposed future work.

- The future work looks reasonable.
- Future work is a continuation of ongoing effort in chemical H_2, pressure vessel, and BOP. There are many practical limitations for a slurry H_2 storage system, both onboard and off-board; therefore, PNNL should consider collaborating with LANL in developing a viable AB liquid fuel formulation.
- The only recommendation concerns the work with alane. The HSECoE's effort to standardize on the same alane, specifically, the ATK macrocrystalline alane that was manufactured in the former Soviet Union, is appreciated. However, the HSECoE needs to ask itself if this alane is truly representative of the alane that will be manufactured on a large scale, should this material pass a go/no-go. The HSECoE also needs to consider if the ATK macrocrystalline alane stands a chance of passing a go/no-go if this form of stabilized alane does not form slurries as well as alane manufactured differently on a large scale, such as microcrystalline with a large surface area and potentially different surface stabilization chemistry.
- The future plans clearly build on past progress and are indeed sharply focused on performance and cost barriers. Sensitivity analyses, component performance validation, and advancements in the level of design detail on a component-by-component basis characterize the proposed work for the coming year. There are still some serious issues with the alane approach that need to be resolved. Perhaps an all-out effort on the AB slurry approach would be the best way to focus activities and resources for the coming year.
- Work should focus on generic rather than materials-specific issues. Because current materials are surrogates, problems specific to AB or alane should be ignored and resources should focus on problems that are common to more potential storage materials should be investigated. Cost analysis, pressure vessel, and BOP issues are good issues for this project.
- The ability to optimize the vessel based on cost with the predictive/cost model should prove to be very helpful. The work cited in the Future Work slide covers the main, necessary areas. The only concern is in the study of the property and behavior effects of the slurries on performance. Validation of slurry system component options is very important. There is concern about the implications of slurry properties on the valves, pumps, and heat exchangers. Optimum slurry properties may conflict with possible operational envelopes for fluid components. Steady-state properties as well as cumulative properties such as particle agglomeration at some fluid system discontinuity or other element need to be understood and considered.

Project strengths:

- The project features excellent experience with solid AB.
- This project has a well organized plan, and a capable and coordinated team.

- The PNNL team has significant expertise to tackle several different areas in H_2 storage, both in analysis and experiment.
- Overall, the relevance, approach, and task planning are outstanding. The quality of the project management and the orchestration of the collaboration activities are also major strengths.

Project weaknesses:

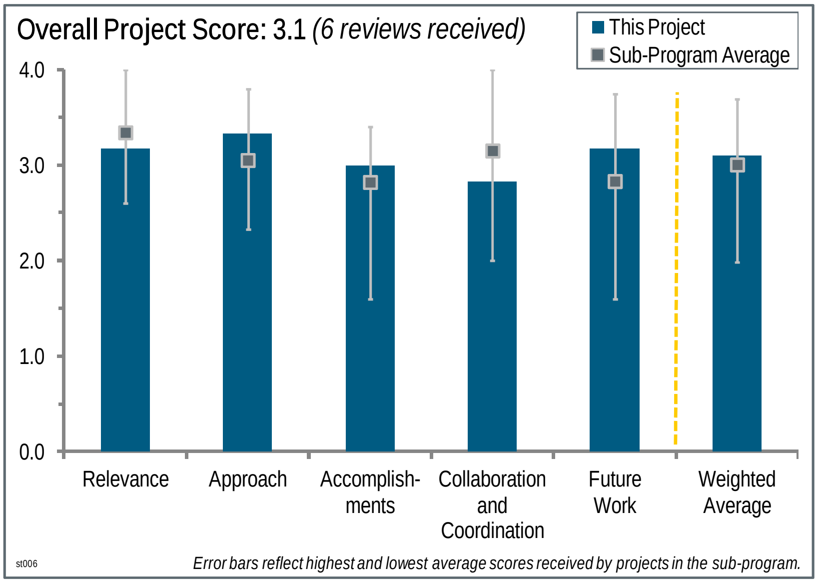
- Slurry fuel formulation may not be practical in many aspects of operation and regeneration.
- There are no significant weaknesses. Accomplishments over the past year were impressive in many respects, but there are still some gaps in the performance area that need to be closed.
- It is not certain that the AB slurry approach is clearly superior to the AB ionic liquid approach.
- The slurry study should lean more toward the science of slurries and less on the art. The current direction seems to focus on bulk slurry properties, with insufficient details on the microscale properties. The project team also needs to study rheology behavior such as viscosity, settling, agglomeration, and flocculation on the particle scale to fully understand issues and mitigation methods. In addition, adding the engineering knowledge related to how slurry properties are affected by the actions of shear flow, valves, pumps, and other components will help in completing the engineering model. Often these elements can deagglomerate, stir, or re-average the slurry to the benefit of the system.

Recommendations for additions/deletions to project scope:

- The researchers should increase slurry study.
- PNNL should consider collaborating with LANL in developing a viable AB liquid fuel formulation.
- Some thought should be given to focusing resources on the best performing chemical H_2 storage material candidate in the coming year to allow more opportunity for achieving validation of all performance targets.
- The presentation indicates that the silicon oil for the AB slurry approach is not the ideal fluid. If not, it would be good to know why not, and what type of fluid is the ideal fluid. The researchers might benefit from an examination of the literature on the colloidal chemistry of non-aqueous media.

Project # ST-006: Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

Bart van Hassel; United Technologies Research Center



Brief Summary of Project:

The prime objective of this project is the design of materials-based vehicular hydrogen (H_2) storage systems that will allow for a driving range of greater than 300 miles. The project makes use of in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials-based H_2 storage systems for automotive applications.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.2** for its relevance to DOE objectives.

- This project is well aimed at DOE Hydrogen and Fuel Cells Program (the Program) targets and barriers. It is an important support component of the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- With no viable materials for storage, the value of engineering analysis on proxy materials is uncertain.
- The development of integrated storage system modeling assists in down-selecting materials systems with the potential to achieve DOE targets.
- This project is investigating the engineering aspects of materials-based automotive H_2 storage systems. Conducting such studies is important to see if a certain H_2 storage material that is promising at the material level will have the requisite performance and weight/volume characteristics needed for use in fuel cell vehicles. One example of the usefulness of such studies is the determination that known onboard reversible metal hydride systems will not meet the automotive requirements. As a result, metal hydride systems have been dropped from further consideration in this project (see slides 5 to 9).
- The United Technologies Research Center (UTRC) provides oversight and also contributes in a major way to an integrated measurement and modeling capability that is profoundly important to the Program. All aspects of the project are fully supportive of DOE research, development, and demonstration objectives. The simulation framework developed and applied in this project allows for quantitative comparison of H_2 storage system options on a common basis and contributes underpinning to go/no-go decisions within the HSECoE.

Question 2: Approach to performing the work

This project was rated **3.3** for its approach.

- The approach is excellent. It focuses on several important problems that must be solved to make an onboard H_2 storage system practical and commercially viable. The approaches are both analytical and experimental, as the individual cases may dictate. Initially all three storage media were considered: reversible hydrides, chemical H_2 storage materials, and cryo-adsorbents. It is important that risk analysis is included.
- The gas-liquid separation (GLS) work is relevant and should be applicable to all chemical storage systems. Ammonia removal is good work that is applicable to systems where acid or base impurities are present. Because the more difficult impurities are unique to ammonia borane (AB), it is probably acceptable to ignore them.
- As a baseline design, the GLS component in the GLS Test Facility looks like it should have considered the potential for slurry particulate problems. It is actually a gas-slurry separator. It would be good to learn what other GLS designs or GLS components were considered in this design.

- The approach was to develop system models for the various types of H_2 storage materials and then compare the performance and other characteristics to the requirements identified as DOE 2017 targets. Such systems were defined to a sufficient level of detail to enable assessment of system performance versus requirements on a common basis for each option. Vehicle, fuel cell, and component models were based on data and process information from one or more project team members and other sources.
- UTRC plays a centralized role in the Integrated Power Plant Storage System Modeling (IPPSSM) team within the HSECoE. UTRC also has responsibility for key aspects of chemical H_2 storage material process operability, H_2 quality maintenance, thermal conductivity enhancement, and failure modes/effects analysis. These are all pivotal engineering pursuits that should serve the greater HSECoE in many illuminating and beneficial ways with respect to refining and optimizing overall H_2 storage system performance.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- Estimation of the tank weight and volume for hydrides based on systems modeling was a key result.
- The improved efficiency of the NH_3 regenerable separator is noteworthy.
- The project has produced reasonable results in compaction. The determination of particulates and control is a significant accomplishment.
- Two qualitatively different metal hydride systems were designed and analyzed, one using only the fuel cell waste heat for H_2 discharge, and the other with an H_2 combustor for the needed thermal energy (slide 6). Based on the available hydride materials (slide 9), it was determined that none of these materials could meet the automotive requirements. For the liquid chemical H_2 storage material option, the major effort was in the design and testing of the GLS, including a failure mode analysis for this component. For H_2 from AB systems, metal-chloride-based systems were found to achieve approximately 10 wt.% ammonia sorption capacity at 25°C. For cryo-adsorption systems using super-activated carbon, mechanical, thermal, and plasma compaction/sintering was examined as a faster alternative to using a binder.
- UTRC has made significant progress toward further elucidating, and to some extent overcoming, one or more barriers to H_2 storage system performance in the past year. IPPSSM contributed to the “diversion” of the metal hydride H_2 storage approach based on the identification of sizable gaps in the material properties needed to meet DOE’s 2017 H_2 storage targets. There had been some encouraging progress reported for H_2 purification, activated carbon compaction, and metal-organic framework-5 (MOF-5) thermal conductivity enhancement; ground work has been laid for GLS validation tests. A substantial portion of the important, planned laboratory experimentation for the current fiscal year (FY) remains to be done in the latter quarters of FY 2012.
- Consistent with the level of funding for this project, a large number of good and useful results have been generated. The project’s modeling results on reversible hydrides have helped to determine that this family of materials is not likely to meet the DOE 2017 system targets for onboard storage, and have thus helped make the way for this family of media being removed from the HSECoE. This is a very useful result. For other good results (e.g., liquid-gas separation, NH_3 removal, particulate removal, MOF composite compaction, and conductivity enhancement), it would be good to see more preliminary thoughts as to practicalities for a real system—in particular, cost and complexity.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.8** for its collaboration and coordination.

- Although several collaborators are listed, the nature of collaboration is not obvious; in other words, it seems to be within information sharing.
- This project is based at the HSECoE. The multiple team members in the HSECoE include industry, national laboratories, and a university, and these team members bring multiple viewpoints to bear on work. The regularly scheduled face-to-face meetings (see slide 18) help to enhance effective interactions among the team members.
- Close, well-integrated collaboration seems to prevail throughout the HSECoE, and this is likely as true for UTRC as it is for other HSECoE partners. However, unlike most of the other HSECoE partner presentations, this aspect of the UTRC effort was not clearly elaborated on in the UTRC presentation.

- The HSECoE partnerships were briefly listed, but they were not discussed in much specific detail. With a few exceptions, the slides list mainly UTRC. Given the joint publications listed in the reviewers-only slides, there must be more detailed collaborations that can be provided.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The proposed future work is reasonable.
- Given the high cost and low efficiency of AB regeneration, the HSECoE should consider dropping the AB work.
- Future work is limited to only one slide (slide 18) that seems to basically reflect a budget-revised operating plan. It would seem that a full analysis of the results obtained thus far should imply some other changes in direction to maximize the value of the project.
- The plan for work in the coming year (as displayed in slide 18) is well conceived, and all the tasks are sharply focused on mitigating H_2 storage system performance barriers. It is recognized that UTRC did have to restructure its work plans after the “diversion” of the metal hydride storage approach.
- The concept of expanding the system models developed for hydrides into cryogenic and chemical H_2 storage materials seems to be missing. It would be helpful to focus on this and the failure mode and effects analysis (FMEA). With regard to H_2 quality research, it is recommended to communicate with companies and institutions that specialize in this technology in order to accelerate the progress and establish feasibility of having the impurities at levels within polymer electrolyte membrane fuel cell tolerance.

Project strengths:

- The system modeling and experience with metal hydrides tanks are strengths of this project.
- This project features good engineering analysis by a strong team.
- Excellent analytical and engineering skills are incorporated in this project.
- The different H_2 storage options are being analyzed in a similar manner to allow for performance comparisons on a common basis. The various team members have different types of expertise, which helps to identify issues in the design or analysis. The FMEA is worth doing for critical components, even at this early stage of system development.
- UTRC has the expertise, experience (especially in H_2 storage development), and facilities to perform effectively as a key partner in the HSECoE. The UTRC role in establishing the IPPSSM framework is critical to the success of this important system analysis/validation activity.

Project weaknesses:

- There are several unrelated tasks.
- There is not enough iteration between recent results and changes in future directions. It is unclear if the collaborations are optimum.
- This project has no obvious weaknesses. A chart that clearly reveals how the UTRC effort interfaces with the efforts of other HSECoE partners should be included in next year’s DOE Hydrogen and Fuel Cells Program Annual Merit Review presentation.
- The component and system designs are based on materials whose performance is not quite up to the requisite values yet. The actual materials, when developed, may have properties different from what has been tested. For example, the compaction techniques and thermal conductivity enhancements investigated for super activated carbon may not apply to MOF-based or other sorbent that might be better for the automotive application. Unfortunately, the surrogate materials are the only ones available to work with at this time. Beyond the ammonia mitigation, there was no discussion of the engineering issues related to AB systems.

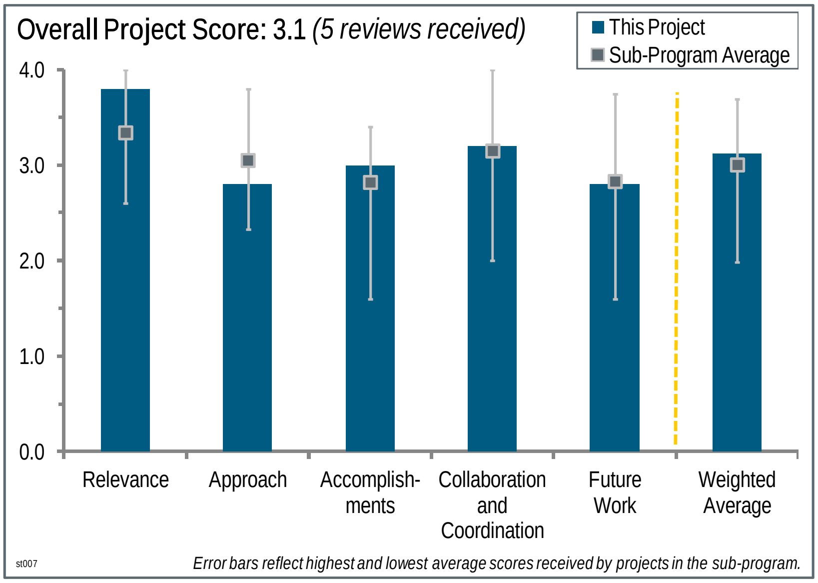
Recommendations for additions/deletions to project scope:

- The scope of activities in this project seems appropriate. Critical barrier issues are being addressed in every task.

- The project team should communicate and/or outsource the H_2 quality work to companies and institutions that specialize in separation technologies. The team should also use current experience with metal hydride system developments and apply it to cryogenic and chemical storage.
- It may be worthwhile to monitor particulate formation with time. Oxide catalysts often produce significant fine particulates in early stages of operation and then show almost zero fine particulate formation for the remainder of their useful lives.
- The only recommendation is that the team should carefully make use of current results to change directions as necessary to provide maximum value to the HSECoE.
- Based on the FY 2012 and FY 2013 plans shown on slide 18, it is not clear if the investigators intend to address the thermal issues related to H_2 discharge in AB systems—the design, configuration, and process control in this reactor are likely to pose significant engineering challenges. The two metal hydride systems shown schematically on slide 6 are configured without an H_2 buffer tank. For AB or other materials-based systems, H_2 will be needed for start-up, and the needed buffer tank should be included in the system configuration (and in weight/volume assessment).

Project # ST-007: Chemical Hydride Rate Modeling, Validation, and System Demonstration

Troy Semelsberger; Los Alamos National Laboratory



Brief Summary of Project:

This project focused on system-design concepts and integration of fluid-phase chemical hydrogen (H_2) storage. The research addressed barriers of efficiency; gravimetric capacity; volumetric capacity; durability/operability; H_2 discharging rates, including start time to full flow and transient response; H_2 purity; and environmental, health, and safety barriers. Progress was monitored on chemical H_2 storage technology for necessary features to be advanced and to ensure needed communication across groups and areas.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.8** for its relevance to DOE objectives.

- This project involves both chemistry and system engineering that is critical for demonstrating a chemical H_2 storage material solution for vehicular applications.
- Down-selection of H_2 storage materials has been done for tank fabrication. Two candidates were selected, but solid-state chemical H_2 storage materials and reversible metal hydrides were eliminated. It must be a significantly difficult task, but the team has done a wonderful job.
- This project is a part of the DOE Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center), and thus it is very relevant to the goals and objectives of the DOE Hydrogen Storage sub-program. This project plays a major role in the chemical storage system work within the Center.
- The Los Alamos National Laboratory (LANL) has completed three years on this project as a partner in the HSECoE. The primary objective of the LANL work is to address critical materials and engineering issues in the development of chemical H_2 storage systems that can meet all of the DOE targets for fuel-cell-powered passenger vehicles. The specific roles that LANL covered over the past year include serving as the system architect and lead designer for fluid-phase chemical H_2 storage systems, assessing for H_2 release and degradation of ammonia borane (AB)-ionic liquids (IL) mixtures, designing subscale reactors, and developing purification components to increase H_2 purity as delivered to the fuel cell.
- Overall, this project seems well aligned with the DOE objectives because it addresses many of the key barriers. The work on AB slurries is comprehensive, addressing a number of key issues from capacity, durability, rates (H_2 release and viscosity), purity (through scrubbers), and safety. The only criticism is that this project is somewhat narrowly focused, because it only involves AB slurries. This is really more a criticism of the HSECoE, not this specific project.

Question 2: Approach to performing the work

This project was rated **2.8** for its approach.

- There must be some variation in the target, but the team has down-selected the materials exactly according to the DOE targets.

- The approach used in this project included a down-selection process resulting in the discontinuation of several research areas to allow focus on reaction characteristics, chemical compatibilities, and subscale reactor design.
- Building on its expertise as a co-leader of the Chemical Hydrogen Storage Center of Excellence, LANL has led the work within the HSECoE to develop AB storage systems. After extensive assessments and review, liquid-based solution or slurry is being continued by the HSECoE. LANL actively participated via internal modeling and contributing to analyses by other HSECoE partners. Good attention was paid toward developing systems that could meet DOE targets.
- It would have been clearer to present the reaction characteristics results in a table showing quantitative results in the different solvents. The rationale behind the solvents tested was not presented. There was no way of knowing how many different solvents were tested and if any trends were noted or established. Solvent effects have a huge impact on chemistry, and a discussion would be preferred. It also would be good to see the measured weight percent H_2 from each run, along with the impurities. It is incongruous to say “no physical degradation of bladder material when exposed to various AB compositions.” Also, the presenter should be specific instead of using useless terms such as “various AB compositions” and then later say that the project team should quantify chemical and physical changes to bladder material. There should be a more technically sound method for determining slurry stability than letting a vial sit for two months and eyeballing the amount of settling. It is unclear how the reactor design shown on slide 16 addresses issues 1–3, and whether it was necessary to do a failure modes and effects analysis (FMEA) to know that reactor fouling is a potential failure mode. It is also unclear why tetraglyme is seen as a solvent in the reactor design but not mentioned in the slides on reaction characteristics. It would be good to know which adsorbents were tested for borazine and why, and whether it was demonstrated that the adsorbed material was not pyrophoric or dangerous when exposed to air and moisture, as will need to be done on a commercial scale if these systems go forward. It is not enough to prevent it from killing the stack; it has to be rendered non-toxic and safe to the consumer in the event of exposure. The literature shows that silica and alumina will adsorb borazine. It would be good to know how these materials compare with zeolites and the others mentioned on slide 21, and whether they were tested. It is unclear what the evidence is that chemical modification of an adsorbent will help meet the borazine scrubber HSECoE mass targets. Overall, the presentation only did a fair job of showing technical data supporting the claims in the summary and on what basis the down-selections, discontinuations, and go/no-go decisions were made.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- The down-selected adsorber and liquid-state chemical H_2 storage materials have some difficulties to fabricate an onboard storage tank. The adsorber requires a liquid nitrogen temperature, and the liquid-state chemical H_2 storage material (AB) requires a process for the regeneration of spent fuel.
- Progress has been significant during this period. Programmatic “Specific, Measurable, Achievable, Relevant, and Timely” (SMART) milestones have been satisfied, and contributions to the total Center team effort have met expectations.
- It is unclear if everyone knows what SMART milestones are. It would be nice to show a table quantifying progress toward milestones similar to what is seen in other presentations.
- A number of accomplishments were made this past year, including the determination of mass loadings and viscosities, the characterization of gaseous-side products, and AB-slurry and slurry-tank chemical compatibilities. The project has overcome one critical barrier by identifying a slurry liquid that remains liquid after dehydrogenation. The progress seems to be well focused and aligned with the overall objectives of the project.
- LANL has conducted extensive experimental screening tests on AB-IL candidates that meet or nearly meet the 2017 DOE storage targets. LANL assessed numerous materials and has discontinued or made no-go decisions on the marginal ones. LANL also continued efforts to identify reaction conditions and compositions that could reduce the formation of ammonia and the very detrimental boron impurities. The laboratory identified reasonable solutions and research pathways to address degradation and performance issues well within the spirit and scope of the HSECoE Phase II work plan. The system architect successfully led an FMEA and developed plans to alter formation of detrimental products during the exothermic decomposition reactions of the AB-IL systems. Limited attention was paid to the endothermic chemical H_2 storage materials, such as alane.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- This project features extensive collaborations with other Center members and, in addition, other external groups.
- Hopefully it was just an oversight that the presenter did not do an adequate job showing what was done at LANL and what was done by the collaborators.
- This project has a number of internal and external collaborators, and the work seems to be well coordinated with other efforts.
- Collaboration with other national laboratories, universities, and industries is significantly important for down-selection as well as the future work. To start collaboration with an expert of social modeling is also suitable for the DOE Fuel Cell Technologies Program.
- LANL has worked very well with various HSECoE partners and other organizations, leading to advances in predicting, down-selecting, and improving performance of chemical H_2 storage media. The tasks appear to have been well coordinated and of great mutual benefit.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- The principal investigator (PI) would benefit from some mentoring so the plans are approached in a technically sound, focused manner, and/or so the PI learns how to present the results more clearly.
- Proposed future activities are a logical continuation of the current tasks that have been vetted by Center members and management.
- Because slurry contains liquid, both volume and weight H_2 densities are unfavorable for onboard H_2 storage. In addition, diffusion of H_2 in the liquid is significantly slow. This must be considered in the future work.
- The plans build on progress and continue to address key issues. It is nice to see that reactor fouling and impurities will be investigated for both alane and AB slurries. Purification will likely be critical for AB slurries—significant improvements are necessary.
- LANL has given a comprehensive plan to perform validation testing of conceptual reactor designs and several other important components such as gas/liquid phase separators and H_2 purifiers for the liquid-based AB media. It is good that much attention is being focused on understanding the formation of harmful boron impurities during storage and decomposition reactions. There are no plans for considering other kinds of chemical H_2 storage materials such as alane slurries, though. It would be an oversight for the Center not to make any effort.

Project strengths:

- This is a very important aspect of the HSECoE.
- This project made a number of nice accomplishments this year. The project is well integrated with the HSECoE and is showing good progress.
- The team has down-selected materials for the next step. It is significantly important but must be very difficult.
- One strength is the use of an FMEA to identify reactor fouling as a potential failure mode.
- LANL has brought very capable technical personnel into the HSECoE team who provided sound theoretical modeling and materials characterization of chemical H_2 storage materials, especially AB. A good balance was made between modeling and experimental assessments. Very comprehensive assessments were conducted for liquid AB materials/reactors during this Phase II stage of the HSECoE project. The knowledge and experience of the former Chemical Storage Center of Excellence was an excellent capability in all of the HSECoE tasks.

Project weaknesses:

- Because slurry contains liquid, both volume and weight H_2 densities are unfavorable for onboard H_2 storage. In addition, diffusion of H_2 in the liquid is significantly slow. At present, these issues are not considered.
- There are no issues with the breadth of effort and innovations for the several components for chemical H_2 storage systems. However, nearly all of this effort has been on AB, with virtually no attention being given so far to other exothermic or endothermic (e.g., alane) H_2 storage materials.

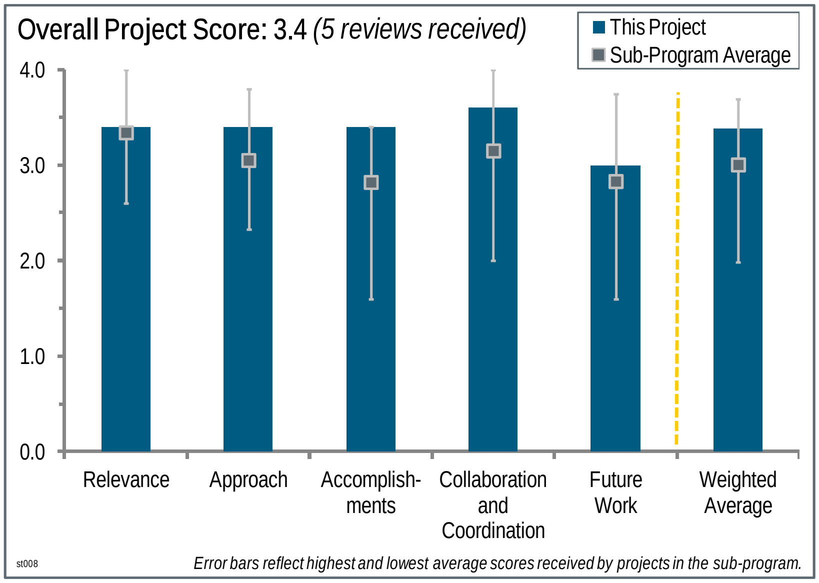
- It seems somewhat premature to spend so much time and energy designing tanks with this level of sophistication. Many assumptions are being made that lead the engineers down a path that in all likelihood is not ideal or universal. This type of project should only be done with strong feedback from the materials research community (which was the plan before the Materials Centers of Excellence were cut). It is very hard to imagine that optimal tank design for AB is similar to that for alane. The other important issue that was not discussed is regeneration. Obviously, the regeneration work lies outside the scope of this project, but it seems hard to justify so much attention on AB without first solving this key problem.

Recommendations for additions/deletions to project scope:

- There are no recommended deletions. To add minor research on other types of H_2 storage materials is recommended to avoid some risks in the future.
- LANL should proceed with the verification testing activities as described in its future plans. Continuing efforts should be made to devise and demonstrate more efficient and regenerable H_2 purifiers with an emphasis on the diborane and borazine species. However, it would be best to develop AB materials that do not form these impurities during aging or H_2 release. Finally, it would be good to see a single slide given in the main DOE Hydrogen and Fuel Cells Program Annual Merit Review presentation that is a direct comparison of the attributes and limitations of the "best/most promising" exothermic AB-IL materials with the endothermic AlH_3 slurry prepared by the chemical systems architect, rather than several slides buried in the reviewers-only section.
- Purification remains an important issue for AB—borazine scrubbers need to be improved by a factor of 2–4. Ammonia scrubbers were not mentioned much, but they will probably need to be improved as well. At this early stage in the development of chemical H_2 storage materials, it will probably be useful to continue to explore a variety of tank configurations for a few different materials: $LiAlH_4$, alane, and AB. Each has its unique advantages and disadvantages and will therefore have different optimal tank designs. One could design a single tank that works for all three, but it will likely be suboptimal in all cases.

Project # ST-008: System Design, Analysis, Modeling, and Media Engineering Properties for Hydrogen Energy Storage

Matthew Thornton; National Renewable Energy Laboratory



Brief Summary of Project:

Vehicle performance objectives for this project are to: (1) develop and apply a model for evaluating hydrogen (H_2) storage requirements, performance, and cost trade-offs at the vehicle system level; and (2) provide high-level evaluation (on a common basis) of the performance of materials-based systems. The energy analysis objective for this project is to perform H_2 storage system energy analysis to evaluate well-to-power-plant efficiency, energy requirements, H_2 cost, and greenhouse gases emissions.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.4** for its relevance to DOE objectives.

- This work provides good information for the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center).
- Comparisons of the various H_2 storage systems in relation to overall vehicle considerations are very important.
- Vehicle performance modeling and energy analysis efforts serve as important links between storage requirements and higher-level systems and objectives. Characterization of media properties provides a clear common basis for subsequent work by collaborators.
- This project provides a pivotal performance assessment function that allows the HSECoE to evaluate progress toward meeting the overarching goals of the DOE Hydrogen and Fuel Cells Program (the Program). All aspects of the project align with DOE research, development, and demonstration objectives. This work is absolutely essential to the task of validating the progress made by the HSECoE.
- The National Renewable Energy Laboratory (NREL) project focuses on the impact of storage/delivery system design, including media engineering properties, on vehicle performance. Although there seems to be considerable overlap with other efforts in the HSECoE (especially the vehicle and onboard storage parameter modeling and storage system and manufacturing cost projection work in ST-010), this project provides the HSECoE with tools to evaluate storage system designs on a common vehicle platform. In that sense, it supports the overall goals of the HSECoE.

Question 2: Approach to performing the work

This project was rated **3.4** for its approach.

- The vehicle model approach looks excellent. Basically, the energy analysis employs the Hydrogen Analysis (H2A) configuration. It is unclear if there is anything better than H2A, or if H2A is good enough for what is needed.
- The vehicle modeling approach is good—it is incorporating different storage systems readily, and validation efforts have been performed. The approaches for the remainder of the efforts appear adequate.
- The approach involves the development and application of a vehicle-level performance model that allows the HSECoE to evaluate alternative H_2 storage materials/concepts in a realistic, self-consistent manner using a

common platform with uniform assumptions. The scope of the modeling framework is impressive, as is the way the analyses link up with other relevant vehicle performance models (i.e., Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation [GREET] model; H2A model; and others). In addition to the trade-off studies and energy analyses that come from application of the model, the project also addresses selected engineering issues that are relevant to adsorbent-type H_2 storage media.
- The scope of the overall approach is too broad to provide information that will effectively guide the HSECoE effort. Very high-level system modeling is used to formulate and evaluate H_2 storage requirements and to analyze well-to-wheels energy performance. In addition, there is a seemingly unrelated task that focuses on "media engineering properties." By extending the project across such a large analysis space, the investigators risk an overall dilution of effort and a loss of focus that does not provide much benefit to the Center. There is overlap between the system modeling approach used in this project and the approach adopted in ST-010. Likewise, there are numerous material assessment efforts being conducted in the Center that overlap strongly with the approach used here. It would have been helpful if the work on this project had been distinguished from the other efforts.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.4** for its accomplishments and progress.

- This project has vehicle modeling analysis for compressed H_2 tanks and some results for the metal hydride, chemical H_2 storage materials, and adsorbent materials systems, as well as some activated carbon results.
- The accomplishments in this project for the past year are excellent. The model development is as comprehensive as it can be after taking into account the present state of H_2 storage system development and operational experience within the HSECoE. Slides 15 through 20 of the presentation display types of numerical information that give highly useful insights and guidance about where H_2 storage system development stands and what needs to be addressed in future work. The results say that a 200+ mile range passenger vehicle is within reach.
- The development of the vehicle model Hydrogen Storage Simulator (HSSIM) that can be used to evaluate storage systems on a common vehicle platform has provided useful and important new information. In addition to the existing slides that present the results of the HSSIM modeling, a slide that summarizes the conclusions and provides recommendations for future Center work would have been useful. The results on H_2 delivery from an alane-based subsystem are also interesting and potentially useful for guiding further work in the Center.
- The fixed volume vehicular modeling is an improvement over the constant available H_2 approach. Some vehicular performance measures have not only targets, but also minimum thresholds; the prime example of this is vehicle range. Below a certain level, the system would not be considered regardless of performance or cost. Storage system cost should be presented. A better description of accomplishments in the energy modeling area is needed. More emphasis on key takeaways in the material characterization accomplishments is needed. It is not clear how the accomplishments presented are important or where they could lead.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.6** for its collaboration and coordination.

- This project features excellent collaborations with other organizations.
- The project has important collaborators from industry and academia, with important contributions being made by the collaborators.
- The collaboration structure is indeed outstanding. The connections with HSECoE partners and with other institutions that provide companion analytical models and supporting data are seamless.
- Slide 23 does a good job showing the expertise that each partner brings to the project. What is not clear is how they manage the collaboration; for example, it is unclear what sort of team meetings are held and how communication is managed, among other issues. So while the team probably deserves a 4 on this, the score has to be downgraded to a 3 because of the uncertainty.
- Collaborations with multiple HSECoE partners are evident, and those interactions strongly support the technical effort in this project. It would have been helpful if the specific contributions from the individual partners had been described. That would have allowed the role played by NREL to be clearly identified and areas of overlap within the HSECoE to be clarified.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future work is relatively straightforward and described adequately.
- The future work plans basically continue what the project team has been doing.
- The proposed future work is spot-on in every respect. Next year's DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) is worth looking forward to. The simulation results should provide a bevy of seminal new insights about where things stand for fuel-cell-powered cars.
- The future work is stated in such a general way that it is difficult to fully assess what will actually be accomplished. A straightforward and clearly stated set of milestones would be helpful. Likewise, a brief presentation of technical barriers and plans to overcome them would greatly aid the ability to assess the future work plans.

Project strengths:

- One strength is the analyses of H_2 storage system impacts on the global vehicular system.
- NREL has a solid vehicle performance modeling capability. The development of the HSSIM is a strong aspect of the project.
- Vehicle modeling aspects provide an important bridge between storage system characteristics and overall requirements and target evaluation.
- This project is an invaluable asset to the HSECoE and to the Program, and it is being done with exceptional thoughtfulness and skill. There is seamless integration of this project with the other contributing projects within the HSECoE. The presentation of this project at the 2012 AMR was very well done.

Project weaknesses:

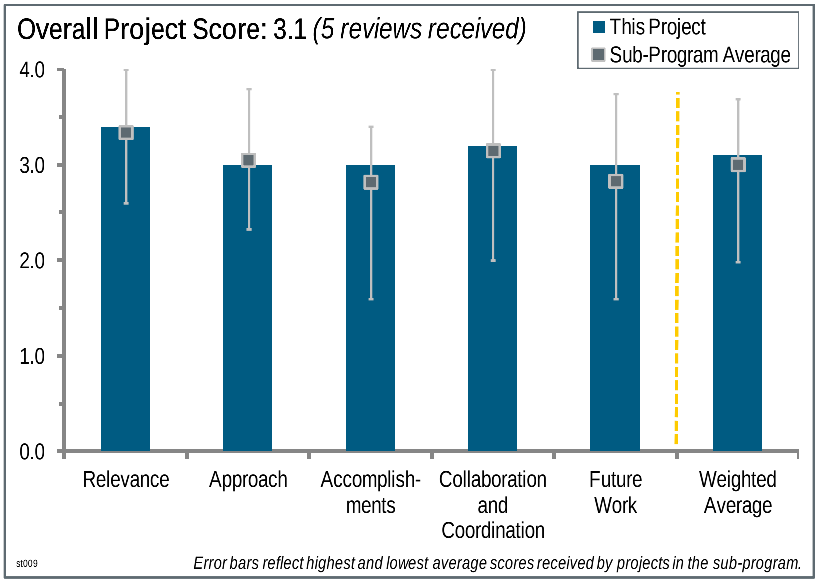
- The modeling approaches use what has been developed in the past. There is nothing new.
- More detail regarding the activities in the material characterization and the use of the results by others is needed.
- An average of the 2011 and 2012 budgets for this project (which should tell approximately how much funding was applied to the project since the 2011 AMR) is $215,000. That is not much at all for a project focused on what this one is trying to accomplish. In addition, NREL also performs some experimental activities within the HSECoE, presumably out of this same budget.
- The (limited) materials assessment work seems disconnected from the modeling/analysis work on the project. The overlap between the vehicle modeling and materials evaluation work in this project and others in the Center needs to be clarified.

Recommendations for additions/deletions to project scope:

- It is unclear what fraction of the funding for this project goes into the material engineering aspect. Perhaps the NREL effort should be fully focused on modeling and simulation. This is not to say that the materials work is unimportant; it is more to emphasize how important the analysis work is. In the future, the project team should please define all acronyms on first use. There are many acronyms in the slides that were not defined. This was actually the case for most of the HSECoE presentations.
- A thoughtful discussion should occur between the principal investigator and the coordinators/director of the HSECoE to ensure that unnecessary duplication and overlap of effort with other projects in both the modeling and materials evaluation areas is minimized. The materials effort is largely distinct and disconnected from the modeling/analysis work. In addition, the materials effort lacks the kind of rigor and scope that is needed to be beneficial to the Center. A detailed review of the materials effort on this project should be conducted in the HSECoE, and mid-course corrections should be made as appropriate.
- This reviewer had no recommendations.

Project # ST-009: Thermal Management of On-Board Cryogenic Hydrogen Storage Systems

Darsh Kumar; General Motors



Brief Summary of Project:

The objective of this project is to address the barriers of system weight and volume, energy efficiency, charging and discharging rates, and thermal management of hydrogen (H_2) storage systems by studying: (1) discharge thermal management for adsorbent systems; and (2) how differently sized and shaped cylindrical pellets affect H_2 adsorption. The project also includes the measurement of engineering properties and the design and fabrication of a three-liter cryogenic adsorption test vessel.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.4** for its relevance to DOE objectives.

- This project focuses on modeling thermal management in adsorbents to gain insight into the balance of thermal diffusion and H_2 diffusion.
- The projects addresses tank heat management, which is necessary to help determine materials feasibility.
- This project is helping to develop a usable cryo-adsorbent H_2 system—one of the few options for storing H_2 onboard a light-duty vehicle.
- This project is in the Hydrogen Storage Engineering Center of Excellence (HSECoE); therefore, it is relevant to the basic goals and objectives of the Hydrogen Storage sub-program. In particular, this project is the lead for thermal management of cryogenic storage systems, which is a critical component of the total absorbent storage system.
- This project addresses a critical aspect of the H_2 storage system. The entire work scope fully supports DOE's research, development, and demonstration objectives and is essential to achieving the goals of the HSECoE. Heat transfer and thermal management will have to be optimized to the fullest extent possible because they profoundly influence time scales and efficiencies and can have an impact on just about all of the barriers being addressed by the HSECoE.

Question 2: Approach to performing the work

This project was rated **3.0** for its approach.

- The modeling approach is reasonable and allows for presenting solutions to tackle heat management issues.
- This is a good plan and approach for achieving the goals and objectives of this project. The focus is on system simulation models and materials properties to support system design.
- The approach involves using system simulation modeling to aid in the design of heaters for adsorption systems for two scenarios and two cases. There was some mention of using failure mode and effects analysis (FMEA), but the connections between the analysis and the modeling were unclear.
- The overall approach is well orchestrated and concisely focused on the key thermal management issues that have been identified within the HSECoE for adsorption-type H_2 storage materials. The integration of transport models with simulation results and with results from direct experimentation is done in a well-considered manner.

- The approach of identifying material properties and then using them in a model simulation, followed by experimental validation, is the right sequence, but time-wise it seems weighted too far on the material properties and modeling efforts and not on physical testing. If the testing does not simply validate the model, and the data shows results different from the model, then the approach of only validating the model becomes an iterative process.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- One accomplishment was using modeling to compare hot gas recirculation to electrical heating with coils. Modeling gave insight into optimizing heat transfer and mass transfer in sorbent pellets.
- Good progress has been made toward achieving system design and definition goals. Design parameters have been identified that allow optimization of system performance. A test vessel has been designed and built, including instrumentation required to evaluate system performance.
- Significant progress has been made toward elucidating the factors that most heavily influence thermal management in adsorption beds and toward providing solutions to some of the apparent barriers. Examples include the helical coil heater approach, the influence of pellet size and shape, and the consequences with respect to refueling time. A cursory look at the "Technical Back-up Slides" showed that there may be some serious issues for metal-organic framework-5 (MOF-5) with respect to pellet durability and thermal conductivity.
- The helical coil heater approach for the cryo-tank is interesting; however, it ultimately concludes that an optimized heater is necessary to determine tank H_2 volume and mass density loss, and hence establish feasibility.
- In general, the accomplishments so far represent important progress toward DOE's goals, if physical feasibility is proven experimentally. One concern is related to the potential thermal modeling of the pellet and how meaningful it will be in predicting the thermal behavior of a packed bed convolved with a heat exchanger and variability in gas flow patterns, among other things.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- There are outstanding collaborations with other HSECoE partners.
- There appears to be good coordination among partners and they seem to have collaborated well, but it was not completely clear from the presentation.
- It would have been helpful to hear more details about the similarities and differences of the work being done by Savannah River National Laboratory and General Motors (GM). One assumes that the project team will need significant discussions with Oregon State University (OSU) on the Modular Absorption Tank Insert device.
- Clearly, the GM staff working on this project are appropriately connected with partners in the HSECoE that are working on closely related modeling and data development activities directed at adsorbent-type H_2 storage materials properties, system design issues, and FMEAs.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The plans for future work are a logical continuation of current activities. Testing of the cryo-adsorption vessel is critical to the project.
- The future plans do address critical barriers and should result in important information and designs, but at the pace of the project so far, the future plans look like they would exceed the time available. The cryo-adsorption vessel testing will be more than a simple model validation and will require time to iterate.
- For the work focused on heating to desorb the H_2, it will be interesting to see the results on cooling and how this couples with various heating scenarios. Also, experimental results from the three-liter system will be great to benchmark models.
- The future plans for this project logically build on progress in the past year and are sharply focused on critical H_2 storage system performance barriers. Based on the results presented by this project, one gets the feeling that as

the studies of thermal management and its effect on component efficiencies progress, the task of meeting DOE H_2 storage system targets could become even more daunting than currently perceived.
- It is recommended that GM consider the cost and challenges of pellet manufacturing as designs are being proposed, and that the team optimize tank design with modeling prior to test-bed-based testing. For example, tank heat distribution and its effect on sorbents is a difficult issue that needs to be examined closely.

Project strengths:

- This project features a strong and well-qualified team. Extensive collaborations have supported and benefitted the project's accomplishments.
- The strengths of this project include the team's strong capabilities in modeling and knowledge of system requirements.
- The approach to thermal management issues within the HSECoE seems to be well organized. The design activities, modeling efforts, and experimentation appear to be well integrated and focused. GM is certainly holding up its end in this task.
- Despite the other concerns in this review, this project has a good approach and elements of the project have achieved important results.

Project weaknesses:

- The collaboration with other HSECoE members working on heat management—for example, OSU—is not visible.
- The potential use of liquid nitrogen for the adsorption heat exchangers should be avoided, if at all possible. Methods for more completely discharging H_2 should be explored. Leaving behind approximately 6% of the stored H_2 is a serious inefficiency.
- This particular project does not exhibit any tangible weaknesses. The thermal management picture for MOF-5 may show some serious deficiencies with respect to target-level performance.
- One weakness is the absence of experimental validation of the modeling effort. There is a good chance that when the three-liter vessel is tested with a heat exchanger and a pellet bed reflecting the analytical model designs, there will be differences from the model. This would suggest the need for at least an iteration on the model and a new physical version of the three-liter vessel or heat exchanger and the pellet stack or pellet configuration. It is unlikely there is enough time for that.

Recommendations for additions/deletions to project scope:

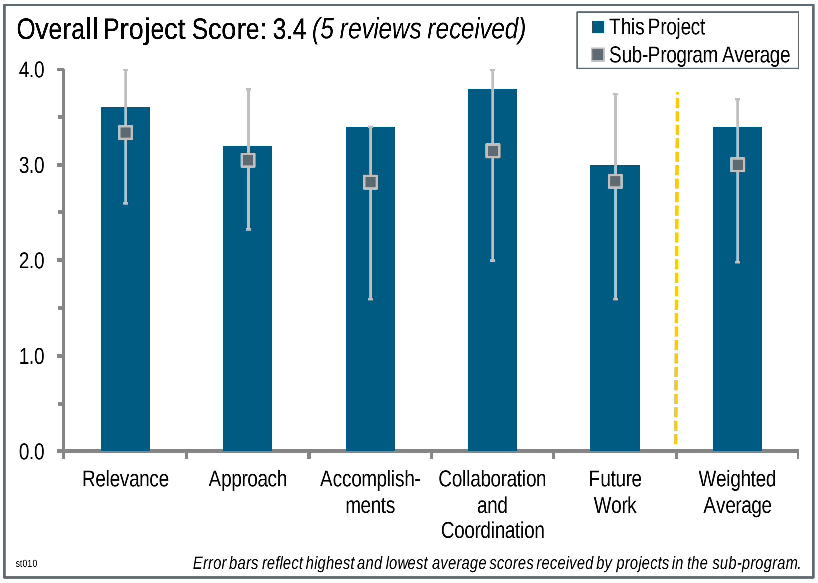
- The scope, overall approach, and plans for the coming year are well thought out. There is no need for change.
- It is recommended to focus on optimization of the proposed heater design using modeling prior to test bed measurement. Another recommendation is to have closer collaboration with other HSECoE team members working on heat management, such as OSU.

Project # ST-010: Ford/BASF-SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

Mike Veenstra; Ford Motor Company

Brief Summary of Project:

The objectives of this project are to: (1) develop a dynamic vehicle parameter model that interfaces with diverse storage system concepts, (2) develop robust cost projections for storage system concepts, and (3) devise and develop system-focused strategies for processing and packing framework-based sorbent hydrogen (H_2) storage media. The models developed for tasks 1 and 2 support the determination of overall vehicle cost and performance as well as enable storage concepts to be exercised at a real-world level. Task 3 supports the creation and validation of sorbent bed models and aids in trade-off analyses.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.6** for its relevance to DOE objectives.

- Sorbents may be the most promising materials-based H_2 storage strategy. These efforts will clarify issues around the use of sorbents.
- This project is a part of the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) and, as such, it is relevant to the goals and objectives of the Hydrogen Storage sub-program. Ford Motor Company is a technology lead in several important technical and organizational areas, including their role as sorbent system architect.
- The project plays a number of key roles in the HSECoE, and thereby strongly supports the DOE Hydrogen and Fuel Cells Program's (the Program's) objectives. Storage targets are implicitly considered.
- This project provides a vital connection between the HSECoE, DOE, and a large automobile manufacturer. Vehicle parameter modeling, manufacturing cost modeling, failure mode and effects analysis (FMEA), and adsorbent system architecture coordination activities serve as useful adjuncts to the main technical task on characterization and optimization of framework-based H_2 storage media. This project is an important element in the overall HSECoE engineering activity and is closely aligned with the objectives of the Program.
- Ford's role in the HSECoE is to develop a dynamic vehicle model that interfaces with different storage concepts, develop cost projections for these concepts, and devise strategies for packing framework-based sorbents into system containers. These roles are very relevant to the HSECoE effort and to the DOE goal of developing materials-based storage systems. It remains to be seen if metal-organic framework-5 (MOF-5) can approach the DOE targets close enough to reach a "go" decision for Phase III.

Question 2: Approach to performing the work

This project was rated **3.2** for its approach.

- The adopted approach involves several crucial activities such as identifying performance gaps, developing processing-structure-property relationships, and material characterization.
- Ford has identified critical issues around sorbents and is systematically addressing them. Data is being supplied to modelers as needed.

- The approach to developing processing guidelines and structure-property relationships is well organized and systematic. Thermo-physical data and isotherm data is being developed. Compaction issues and thermal conductivity relationships are being investigated to provide information for the go/no-go decision. Volumetric capacity and thermal conductivity, which have been identified as critical issues, are the focus of the efforts on adsorbents. The integrated system model approach is vital for a complete evaluation against the DOE targets.
- The approach consists of several discrete efforts; each is led by an individual and dovetails into the needs of the HSECoE. There is a good industrial component to the work, which is obviously needed if the overall concept of onboard solid-state storage is to succeed. The effort focuses largely on the MOFs, which are important to the cryo-adsorbent focus of the HSECoE. The FMEA will also be very valuable to the overall HSECoE effort.
- A systematic and well-reasoned approach has been adopted in all three tasks of the project. MOF-5 was selected as a prototype system for framework material characterization and optimization, and a solid experimental approach was used to characterize the engineering properties of the material under different process conditions. However, it is not entirely clear whether the results obtained from the extensive experimental and modeling studies conducted on the MOF-5 system will translate into the predicted performance of improved framework materials that may emerge in the future. There appears to be overlap and duplication between the modeling and cost analysis efforts of this project and the National Renewable Energy Laboratory project (ST-008). It would have been helpful if the technical efforts had been compared and contrasted in the review presentation.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.4** for its accomplishments and progress.

- Ford has made good progress with the MOF-5 material characterization, which is vital to system design and performance modeling. The system design FMEA has identified important potential problem areas during the design process.
- The permeation data is a critical addition to this work and shows promising results. Failure analysis is a very significant addition to the project and has the potential to guide and refine project direction and resource allocation.
- The accomplishments for 2011 are excellent. An engineering property database for MOF-5 was completed, as well as a partial database for activated carbon that is limited by densification challenges. Ford also took on the responsibility of system architect for adsorbent systems in 2011. Ford developed "Specific, Measurable, Achievable, Relevant, and Timely" (SMART) milestones and a Gantt chart to coordinate the work on adsorbent systems across the Center. The architect identified and prioritized research gaps. Ford also verified the integrated system model results for a complete system evaluation against DOE performance targets.
- Good progress has been made in all tasks of the project. The experimental, modeling, and cost analysis results are being transferred effectively to other partners in the project. The expansion of the project to include the coordination of the system architecture work is an important and useful addition. However, it is unclear how that overlaps with the system architecture work in the Jet Propulsion Laboratory project. One concern is that multiple modeling and experimental efforts are being conducted on the MOF-5 system within the HSECoE. This has led to some confusion for the reviewers about the roles and responsibilities of each individual group in the total effort. For purposes of this review, it would have been helpful if the technical work on MOF-5 materials in the Ford Motor Company/BASF-SE/University of Michigan (UM) project could have been put in the context of all of the other related efforts of the Center.
- The project has been active and has produced numerous results. However, the slides were rather compressed, so the individual efforts have probably generated more results than can be shown in this short presentation. The preliminary cost analyses are very useful. The shortcoming of this presentation is the general failure to clearly state how the results have influenced the HSECoE and relate to achieving the DOE targets. For example, it is unclear whether distinct problems have been uncovered that might affect the upcoming go/no-go decision for Phase III.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- The collaboration with complementary research groups is excellent. The collaborators are well qualified and provide valuable contributions to this effort.
- Generally, the collaborations seem to be within the three project partners and interaction with the HSECoE. A few more collaborations might help.
- There are extensive interactions and collaborations with the HSECoE team. Many of the partners in this project made major contributions to the accomplishments and success of the project. In addition, BASF and UM were subcontractors to Ford on this project and supported the progress and accomplishments.
- The close collaboration and synergy among numerous partners in the project are evident. All partners are making significant contributions to the technical effort. Regular exchange of technical and program information is occurring, and good coordination with the overall HSECoE effort is apparent.
- The Center's approach of experimentalists and modelers working closely together is good.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future plans have Ford continuing the important characterizations of the MOF-5 adsorbent and the associated storage system and vehicle modeling. Important in-situ neutron imaging will also be done for model validation.
- Neutron sorption measurements should be used to validate diffusion/sorption models.
- Future work plans aim to fill in the technical gaps to inform the go/no-go decision process for Phase III. They are quite ambitious, but the budget has been increased significantly for 2012. Cost projections are intended but cannot be evaluated against the DOE cost target until the revised target has been established.
- The proposed future work continues the work started without much change in direction, if any. One would expect that some of the findings to date might suggest at least limited changes in directions.
- The future work is clearly stated and focused on the important technical barriers in the MOF-5 adsorbent system and on the continuation of the storage parameter and manufacturing cost modeling work initiated earlier in the project. Although the engineering evaluation of the MOF-5 system is important and fully consistent with the HSECoE goals, it remains unclear whether the results of that work will provide a useful predictive capability that can be applied to improved adsorbent systems that may emerge in future materials work.

Project strengths:

- This project has a strong, committed team with extensive experience and capabilities.
- A strong development and engineering team is conducting the technical work on this project. Excellent progress is being made on all tasks and a solid plan for future work that focuses on critical technical barriers is in place.
- The Ford team has excellent qualifications and the collaborators have significant expertise and experience to bring to the effort.
- This project features good industrial/commercial input. Looking at practical (application) problems is another area of strength.

Project weaknesses:

- This presentation did not clearly define the "effective" H_2 storage capacity (in terms of weight percent) or range of capacities, or indicate how the proposed system will meet the DOE storage targets.
- A large number of modeling and experimental efforts are being conducted on the MOF-5 system within the HSECoE. This has led to some confusion concerning the roles and responsibilities of each individual group, and it seems that some efforts are duplicated. A clear and succinct delineation of the role played by this project within the context of all the other work in the HSECoE is needed.
- This project does not seem to express practical conclusions very clearly; for example, relative to the overall practicality of using MOFs for vehicular H_2 storage.

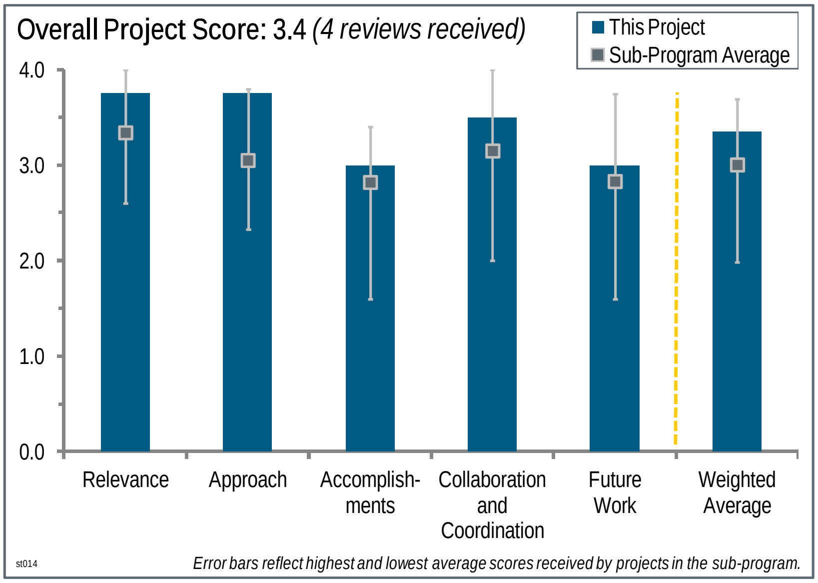
Recommendations for additions/deletions to project scope:

- The project team should focus more on the question, what the results achieved thus far mean, and whether any directions should be changed.
- It would be good to know whether the Center has calculated mechanical forces on pellets/particles due to thermal expansion/contraction of the tank on cooling and warm-up. These forces, along with structural properties of pellets, should give a good estimate of fracture behavior in use.
- Ford should be encouraged to evaluate the prospects of whether a sorbent-based system can be a viable alternative for automotive use and to develop a rationale for continuing research into sorbent materials and systems.
- MOF-5 is not likely to meet the 2017 DOE targets, and it is unlikely that material will be employed in the final engineering embodiment developed in the Center. This project must not simply focus on MOF-5 as the final solution; it should develop the flexibility to incorporate new materials as needed.

Project # ST-014: Hydrogen Sorbent Measurement Qualification and Characterization

Phil Parilla; National Renewable Energy Laboratory

Brief Summary of Project:
The overall objective of this project is to help ensure that capacity measurements for hydrogen (H_2) storage materials are based on valid and accurate results, thus allowing promising materials to be properly identified. To advance the accomplishment of this objective, this project specifically aims to: (1) assist materials research groups to characterize and qualify their samples for H_2 storage properties; and (2) analyze, identify, and recommend corrective actions for major sources of measurement error in volumetric systems.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.8** for its relevance to DOE objectives.

- The accurate measurement of all potential H_2 storage materials plays a critical role in the success of the DOE Hydrogen and Fuel Cells Program (the Program).
- The validation of the material properties proposed is critical to avoiding misleading results.
- This laboratory has spent the past six years refining the techniques necessary for the evaluation of materials behavior/performance in a global research environment that has demonstrated less-than-consistent results. The National Renewable Energy Laboratory (NREL) is now one of the few laboratories that can produce credible results over the wide pressure/temperature ranges of interest to the Program. These capabilities would have been of great value at the start of the DOE Hydrogen Storage sub-program’s three material Centers of Excellence six years ago.
- This project represents a much-needed effort to improve gas adsorption measurements in the DOE Office of Energy Efficiency and Renewable Energy (EERE) portfolio. This should improve material identification and provide reliable isotherms for engineering systems. The dissemination of best practices is appreciated. The project provides a robust validation mechanism independent of the material synthesis laboratories.

Question 2: Approach to performing the work

This project was rated **3.8** for its approach.

- This project features an excellent approach.
- The volumetric and spectroscopic techniques used are the most appropriate for determining materials performance.
- It is hard to criticize the achievements of this project. The project team is taking a logical and necessary approach to the work.
- The approach of identifying the possible error and guiding the material researchers to characterize/qualify their samples is very logical.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- Several major sources of errors have been identified and resolved. The “Best Practices” recommendations will help the researchers to produce a more accurate material-level evaluation.
- It is recommended that this team also be involved in validating the measurements of compacted cryo-absorbent media.
- The efforts of the laboratory have probably been redirected several times over the course of the Program. It has unfortunately taken a long time for the NREL efforts outlined in this presentation to come to fruition. NREL’s effort should be rated closer to 3.5.
- The procedural work is clearly world class and a valuable asset for DOE, and it has been developing throughout the lifetime of the Hydrogen Sorption Center of Excellence. The round-robin effort seem a little late, given that the door has almost closed on the materials development portfolios, but there are indications that there is strong agreement across laboratories, perhaps due to the earlier work. This work should clearly be published, but the best practices document may suffice. Validating adsorption properties has been useful, but clearly even this is being abused in some forms. For instance, in the talk by Northwestern University, where the NREL nitrogen isotherm data was arbitrarily scaled by a factor of approximately 1.2 and then applied to H_2 isotherm data, even though the shapes of the H_2 isotherms are not even similar between the Northwestern University and NREL measurements. This type of practice needs to be guarded against. Hopefully the information Northwestern University gained from this interaction is put to good use.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- This project’s worldwide collaboration is visible.
- The round-robin testing involved several partners, and the measurements are well coordinated between all the partners.
- The collaboration with Northwestern University appears to have worked particularly well in highlighting the analysis errors of that institution. It would have been beneficial for specific data or data analysis to have been presented that outlined in better detail the nature of the collaboration with certain principal investigators (PIs).
- Samples in round-robin testing and external samples measured indicate a solid collaborative foundation and demonstrate a continued need for the measurement/validation services.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The development of new measurement capabilities is necessary and critical to the Program.
- Given what appears to be the direction being taken by the Program, the proposed future work seems appropriate.
- It seems that this project acts in more of a service role, which should be available to EERE-funded projects. In that respect, the details of the future work are sketchy, but understandably so. Perhaps EERE should indicate that NREL is available to its funded projects.
- It is recommended that this project also be involved in validating the measurement of compacted cryo-absorbent media within the Hydrogen Storage Engineering Center of Excellence (HSECoE). Another recommendation would be to lead the validation of results reported within the HSECoE as opposed to just selected samples. A clear, specific plan is missing. It would be helpful to show specifically what materials and testing are planned.

Project strengths:

- This project features capable and experienced scientists with good facilities.
- NREL now appears to be the only laboratory capable of delivering indubitable results, and it is more capable of collaborative work in a professional environment.

- Strengths of this project include the detail of the measurement techniques and the ability to identify errors. Other strengths are the HSECoE collaborative efforts and the measurement validations.
- Strengths of this project include the coordinated effort between multiple institutions and the well-organized "Best Practice" procedures.

Project weaknesses:

- If this project loses funding, the expertise and instrumental capability at NREL will atrophy. Also, there are no clear efforts by NREL to leverage its capabilities to the new projects and to the needs of the HSECoE.
- The development of any new measurement capability will take a lot of resources in general. It will be good for the PI to prioritize the new capability list and rationalize the effort.
- There were no weaknesses.

Recommendations for additions/deletions to project scope:

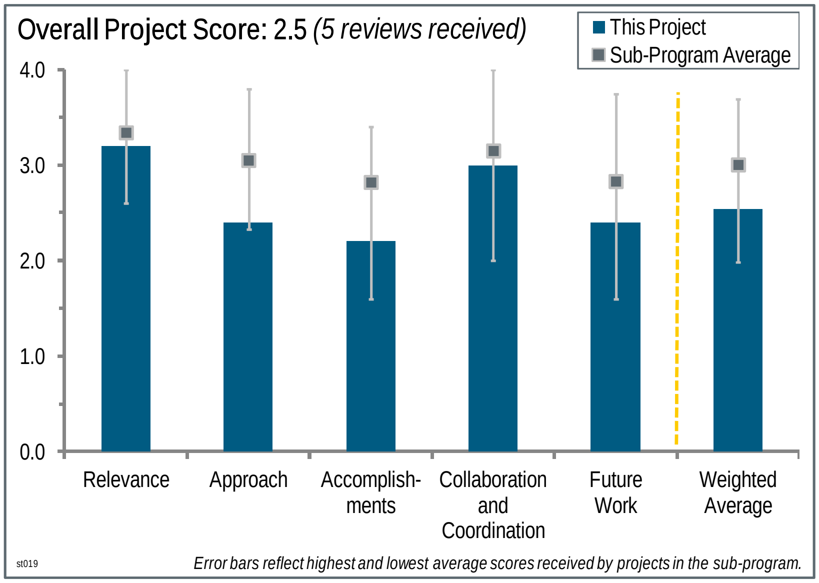
- These facilities should be available to the EERE H_2 storage projects.
- The PI may consider determining the acceptable error bar range in this kind of measurement and make recommendations to materials research groups.
- It is recommended that NREL be involved in validating the measurement of compacted cryo-absorbent media within the HSECoE. Another recommendation would be to lead the validation of results reported within the HSECoE as opposed to just selected samples.

Project # ST-019: Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

Peter Pfeifer; University of Missouri

Brief Summary of Project:

The objective of this project is to address the lack of understanding of hydrogen (H_2) physisorption and chemisorption by: (1) fabricating high-surface-area multiple-surface-functionalized nanoporous carbon (from corncob and other precursors) for reversible H_2 storage (physisorption) with superior storage capacity, (2) characterizing materials and demonstrating their storage performance, and (3) optimizing pore architecture and composition. These tasks also address the barriers of system weight and volume, system cost, charging and discharging rates, and thermal management.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.2** for its relevance to DOE objectives.

- The project is relevant to DOE objectives, in particular reducing the raw materials cost of H_2 storage materials.
- The project aims to attack the key barriers and, if successful, might move the leading edge of adsorption capabilities in some areas. The ability to lower costs is a very important aspect.
- Increasing the binding energy of adsorbed H_2 is critical for this technology from the point of view of materials development. Optimizing the packing of adsorbent material is also important for adsorption storage systems.
- This project is looking at improving the adsorption properties of high-surface-area, porous carbons that are derived from natural products. The project team's primary objective remains to incorporate substantial concentrations of boron into the carbon microstructures in order to increase bonding energies with H_2, while still retaining storage capacities at ambient temperatures and moderate pressures (i.e., up to approximately 100 bar) to levels found when H_2 is adsorbed at cryogenic temperatures. If such storage materials can be developed with sufficiently low costs, more of the DOE storage performance targets might be achieved using adsorption storage vessels. Significant issues still remain with volumetric densities from these boron-carbon materials, even if gravimetric capacities were increased. Higher heats of reactions also negatively impact engineering these vessels for thermal management during both H_2 adsorption and release. The issue of reducing the costs of making and processing these materials over conventional activated carbons was not addressed in any detail.

Question 2: Approach to performing the work

This project was rated **2.4** for its approach.

- While some of the work to understand the role of the dopants seems derivative, the compounds used are new and seem to be providing results. The use of tanks to test the material is excellent. The confirmation of previous speculation with spectroscopic data is good, though there is more to do here.
- The work this year was significantly focused on fundamental measurements and modeling, which may not be justified without a plan to significantly improve the base materials. Some improvements in boron doping have been achieved, but this does not appear to be the main focus of the work as it probably should be. While not

funded by the DOE Hydrogen and Fuel Cells Program (the Program), the engineering test bed does not offer much value to the improvement of materials and may be a distraction.

- The ultimate goal of the boron functionalization work is unclear. Boron substituted within a graphene-like structure seems to be the goal, but the ability to do this appears to rely on a high defect density. Given the overall reduction in surface area of materials that have been exposed to $B_{10}H_{14}$, it would be interesting to know if one can assume that the defect density is low. In addition, the goal should be to generate as many lattice defects as possible in the base material. This approach also seems to be inconsistent with the language of slide 5, where doping the surface rather than promoting the lattice substitution is the goal.
- Using extensive, in-house expertise with boranes (e.g., $B_{10}H_{14}$) to provide novel means for boron additions to the promising carbon host, the University of Missouri team has been able to incorporate boron atoms via thermal processing to minimize the loss of surface areas. A variety of characterization techniques are used to evaluate the impacts of synthesis and processing on the nature and distribution of the pores and the adsorption properties (e.g., capacities and heats of adsorption). During the early phase of the project, computer modeling of pore structures was used to predict the optimal configurations for maximum H_2 adsorption. The more recent focus appears to be on material preparation and characterizations, which is appropriate.
- The doping approach is thorough and methodical, and it goes deep into the understanding of the fundamentals. However, this is done at the expense of good H_2 storage characterization and finding solid proof of increasing binding energy. The project team has only presented a couple of near-room-temperature isotherms to deduce the isosteric heat of adsorption, which is generally high at low coverage, such as the case here. A more convincing demonstration would have been to find the isosteric heat of adsorption at larger coverage by going down to lower temperatures, as the principal investigator has done in the past. It would also be useful to learn whether the doped material is reversible or not.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.2** for its accomplishments and progress.

- Progress is relatively slow; the characterization efforts are an overkill for such little gain. There seems to be a little improvement in functionalizing the adsorbent, but the storage capacity is still very low.
- A low-temperature isotherm shows H_2 uptakes that are similar to most other high-surface-area activated carbons. The still relatively low isosteric heat of 10 kJ/mole will presumably still fail to satisfy the Program goals at room temperature. Regarding the information on slide 9, if a doubling of binding energy increases adsorption in the Henry's Law region, it is not clear why such a large enhancement is also seen at 200 bar.
- Using $B_{10}H_{14}$, carbon samples were doped with approximately 5–10 wt.% boron and were characterized by various methods, including assessing the adsorption behavior of H_2. While some enhancement of H_2 capacity and binding energies were noted near ambient temperature, these improvements still fall far short of the objectives and DOE targets. There did not seem to have been many samples made and characterized during the past year. The methodology used to analyze adsorption test data was not well described, and it was confusing to interpret actual performance observed by this team. It seems to be more or less a shotgun approach as related to the selection of characterization techniques and samples, without a coherent explanation of the project team's observations and the true potential and limitations of these materials.
- Many of the technical accomplishments appear to have been the prior year's work. The work on improving the derivation of the enthalpy of adsorption is very useful, but it is surprising to see that it was only applied to one sample. Developing and testing a variety of methods and parameters for improving boron loading should have been a priority, with enthalpy analysis being used as a tool to evaluate performance.
- Doping the base material without loss of surface area is a good accomplishment, though it would have been beneficial to see much of this confirmed by others. Testing in a multi-liter vessel shows not only the ease of making the material, but also provides interesting results for tank designers. Unfortunately the H_2 storage capacities are low, but that is important for the researchers to learn and work toward better results. The main concern is the actual mass percent improvement of the system based on this developed material, relative to a tank with no media at the same pressure and temperature, may be negative or very small. This is an issue all storage projects need to face. The University of Missouri has taken on this issue, so the team should be applauded for facing the problem, but it needs to test for significant H_2 mass increase due to adsorbent at room temperature. It was good to see the spectroscopic data supporting previous results.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- The group has both national and international collaborations on sample characterization.
- The project features a good set of international collaborations.
- The project has many collaborators, but their contributions are unclear. It is likely that many are just discussions at conferences.
- There was good cooperation with the various University of Missouri departments on producing and characterizing materials. It was less obvious how the theoretical modeling results contributed to the overall project, especially on approaches to dope with boron. Several outside collaborations to obtain specialized characterizations were evident. Hopefully this will be continued, with the addition of other insightful methods such as Raman and solid-state nuclear magnetic resonance of the boron-doped carbons as made and in the presence of adsorbed H_2.

Question 5: Proposed future work

This project was rated **2.4** for its proposed future work.

- The proposed future work is not very ambitious, but it is acceptable.
- The most important result expected from this work is to clearly demonstrate the advantages and disadvantages of boron-doped materials. The pelletizing work seems to be complete.
- Given the results presented here, the heats of adsorption and the surface areas still fall short of the Program goals for H_2 uptake at temperatures of 80 K or 303 K. A number of comments from last year's program review could apply to this year's work. In spite of some apparent improvement in H_2 uptake, these materials seem to have an upper limit of H_2 uptake that still falls short of the Program goals.
- All of the proposed tasks on slide 23 are very reasonable and highly desirable to provide much-needed insight and validation on whether boron-doping can substantially improve the adsorption properties of microporous carbons. However, the prognosis of these materials reaching performance levels needed to achieve DOE targets is poor.
- The focus on new boron-doping techniques is the most promising of the proposed tasks. These materials will not meet DOE goals without large improvements in the base materials. Given the limited resources, that work should not be diluted by fundamental studies or scale-up (monolith) studies without some significant improvement in material properties.

Project strengths:

- The University of Missouri has personnel with great knowledge and expertise with boron chemistry, as well as equipment and experience working on the adsorption properties of porous carbons and other materials.
- Strengths of this project include the low cost of the base stock material and the ability to make and test large batches.
- This project has a methodical and thorough approach and gives a more complete picture of the advantages and disadvantages of boron doping.
- A significant increase in the H_2 adsorption energy with boron doping has been made. The boron-doping process has been improved and doping levels have been well characterized. This is critical for room-temperature physisorption of reasonable amounts of H_2.

Project weaknesses:

- The material developed by this project is far from being practical at room temperature.
- While boron-doping has been improved, not a lot of progress appears to have been made on developing host materials or increasing the capacity to meet DOE goals since the prior year.
- There has been considerable disorder in the approaches used to select and investigate the carbon-boron candidates. Synthesis methods and characterization techniques seem to have been selected mostly for availability at the university or research group, with little discrimination on whether they are the most appropriate to address

the stated objectives and needs. In addition, nonconventional assessments of thermodynamics are given with minimal explanation or justification of their applicability.
- It is not clear whether meaningful added storage is achieved even with the best materials. There is some additional storage, but one must consider only the excess amount of H_2 stored compared to what is in the gas phase. The net H_2 storage with these materials relative to a system with no adsorbent at all is likely to be low.

Recommendations for additions/deletions to project scope:

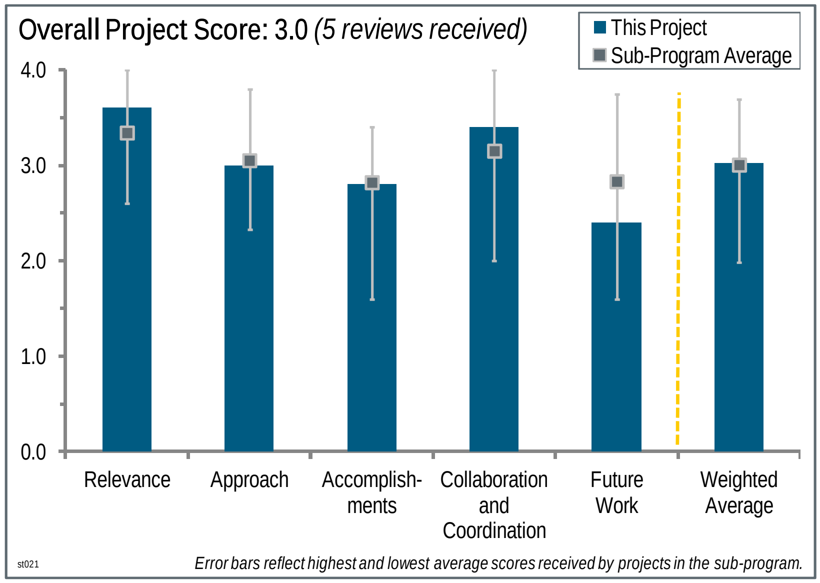
- The researchers on this team should vigorously perform the tasks outlined on their Future Plans slide 23. Their goal should be to validate their claims of better performance from boron-doped carbons and provide experimental insights into changes in structure and chemical bonding within the host sorbent and the nature of the H_2 adsorption process. In addition, thorough characterization of all relevant properties should be made, and the results should be replicated.
- The overall storage properties of the best materials from this project are only a little better than the activated carbon materials MSC-30 or AX-21. Apples-to-apples comparisons should be made. For example, testing should be performed for MSC-30 monoliths compared to boron-doped 3 K monoliths prepared under the same conditions. It seems that efforts would be better spent on improving the current materials than working on engineering scale-up.

Project # ST-021: Weak Chemisorption Validation

Thomas Gennett; National Renewable Energy Laboratory

Brief Summary of Project:

The overall goal of this project is to evaluate the spillover process as a means to achieve U.S. Department of Energy (DOE) 2017 hydrogen (H_2) storage goals. To advance the accomplishment of this goal, this project specifically focuses on four objectives: (1) validating measurement methods, (2) identifying and synthesizing several candidate sorbents for spillover, (3) determining H_2 sorption capacity enhancement from spillover, and (4) observing and characterizing spillover H_2-substrate interactions with spectroscopic techniques.



Question 1: Relevance to overall DOE objectives

This project was rated **3.6** for its relevance to DOE objectives.

- The room-temperature H_2 adsorption is a very attractive technology option for onboard H_2 storage, and accurate measurement is the key to the success of this project.
- Given the diversity of broad disagreement in the scientific community about spillover, this project is vital to bring about consensus.
- This is a critical project for the DOE Hydrogen and Fuel Cells Program because it will establish if spillover is viable in a way that will be hard to debate. With that knowledge, smart decisions can be made on funding spillover work in the future.
- Developing reliable, validated measurements of H_2 stored via the controversial, often irreproducible spillover mechanism is important to DOE to evaluate the future promise, or lack thereof, of the spillover mechanism for H_2 storage.

Question 2: Approach to performing the work

This project was rated **3.0** for its approach.

- Selecting samples with established and standard preparation procedures was a good starting point. At a minimum, it is recommended to expand this work to the samples that are reported with much higher capacities.
- Although ruthenium (Ru), palladium (Pd), and platinum are not practical for real applications, using these catalysts is a good choice for fundamental understanding. It would be nice if the principal investigator (PI) could also indicate how much enhancement one must achieve to make spillover viable for H_2 storage systems based on today's best available materials. It is unclear if it is 15%, 50%, or 100% enhancement.
- Air-stable, synthetically facile materials with a well-established detection limit of 15% are excellent starting conditions. Although the process is both described as chemisorption and hydrogenation (slide 13), something to consider is whether the project team can exclude hydrogenation through calorimetry tests.
- The use of doubters and adherents in all experimental phases is key to having a robust result suitable to inform future research and development program decisions at DOE. The precalibration between laboratories and the use of spectrographic characterization methods to study the effect observed is excellent. This is a model project, in these aspects. The use of a wide set of spectrographic data to try to understand spillover as an H_2 storage process

is also excellent. The project team's only fault is that to get stable materials with fast kinetics, it gave up the possibility of seeing a large enhancement.
- The approach to validating the spillover of H_2 onto substrates was appropriate, with a combination of reproducible sorption measurements and characterization techniques. A criticism of this general approach is that other than the sorption measurements, the spectroscopic measurements tend to be more qualitative, and they are only made semi-quantitative with a lot of hard work.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- The samples are synthesized with well-controlled and repeatable conditions. All of the measurements are well planned and conducted.
- The identification of water (from catalyst reduction) in the measurements was very important. It is recommended to reconsider the reliance on Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurement to establish reversible spillover, given the high noise level.
- Regarding the material presented on the high-temperature activation slide, it would be nice to know whether further heating of Ru-hydrogen bonds converts the metal back to zero valency and releases H_2, or if it merely transfers this hydride to the proximal substrate, altering the system (possibly observed by cycling this system). It was unclear if the PI measured the H_2 released during the 250°C degassing. If the carbon-hydrogen bonds proximal to the Ru catalytic site appear activated for reversible release of H_2, why their absorbance is not shifted should be explained. Carbon-hydrogen bonds that are agostically interacting with metal centers have clear spectroscopic signatures. This is difficult, but for all DRIFTS measurements it would be nice to see positive controls with dosing similar to the proposed unknown measurements, thus instilling confidence in the small "peaks" that are highlighted. In reference to the $RuBC_x$ solid-state Nuclear Magnetic Resonance, if one doses the carbon support with less boron, it would be interesting to see if an intermediate chemical shift (between 5 and 7 ppm) and less broadening is observed.
- The results are good, but perhaps a bit slower than expected. The identification of a potential spectroscopic trace of spillover is good, but until it is understood, there will still be room for doubt as to what is being seen in the spectrographic data. That notwithstanding, the widely agreed establishment of spillover as a real but small (in these systems) phenomenon is a big accomplishment. While the project team chose the samples for the valid reasons of fast kinetics and good stability, none of these samples was likely to offer high-capacity change (4% plus), so the small enhancement is in the order that might be expected. Thus, the goal of estimating if spillover can meet DOE goals is somewhat in doubt; it is too open-ended of a question to prove the goals cannot be met using the spillover mechanism. There is no physical example of the goals being met, and the theory is not dependable based on the wide range of theory results in the literature. It was good to see the rigor in data reduction, such as in the data on the Pd-templated material.
- The progress toward making reliable, reproducible sorption measurements of H_2 spillover on "model" materials has been good. The quality of the measurements gives confidence that the amount of spiltover H_2 is being measured with accuracy and precision. This quantity is unfortunately much lower that the claims of others that inspired this work. Therefore, this work at the National Renewable Energy Laboratory is very valuable in correcting the overly ambitious claims made previously by other organizations. The work falls short in providing adequate, confident correlations of the spectroscopic data given the small amount of spiltover H_2.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- The overall activities involve several partners, and the efforts are well coordinated.
- The fact that this project is inherently a high-collaboration program is why it is a good project.
- Other institutions (e.g., Penn State University) within the Hydrogen Storage sub-program are also conducting related and similar work. It is recommended to consolidate these projects or have clear distinctions between them.

- This project features strong collaborations, especially in the sorption measurements and in improving the sorption measurements that others in the field are performing. The project is a terrific service to the sorption community. The project is well done.

Question 5: Proposed future work

This project was rated **2.4** for its proposed future work.

- The spillover effect has been studied for awhile. A conclusion should be achieved soon in terms of whether this is a realistic pathway for onboard H_2 storage applications. The continued fundamental understanding could be accomplished within the scope of the DOE Basic Energy Sciences Program.
- Granted, the project is nearly over, but it is unclear how "enhancement" measurements will help DOE judge whether spillover materials can meet automotive application targets. It is unclear whether absolute capacities are required, and whether they can be bounded.
- This project looks like good work, but it would have been good to have seen a dependable estimate of what might be possible with spillover.
- It would be recommended to expand this work to include samples reported with the highest weight percent H_2 uptake within the Hydrogen Storage sub-program to prevent continued controversy.
- Based on the current results, which are similar or identical to other reliable researchers, now is the time to develop the best case scenario for spillover of H_2 onto substrates for DOE and other researchers interested in this area. Particular focus should be placed on developing chemically/catalytically realistic, thermodynamically and kinetically reasonable pathway(s)/mechanism(s) to provide a "best guess" of the maximum amount of H_2 adsorbed via spillover at room temperature and technologically useful pressures. The existing future work statement seems to be an exercise without any well-defined endpoints, go/no-go decisions, etc. The stated future plan includes a task to go back into the "materials design phase"; the project team should first have to justify what chemically reasonable pathways can get these materials into the ballpark of achieving the DOE H_2 storage targets before proposing any additional future work. This work should not stray from the goal of providing the storage community with information regarding the ultimate potential for H_2 storage these spillover mechanisms enable; if, as it seems now, there is no path forward, then this line of research should be terminated.

Project strengths:

- This project features a good, coordinated effort between multiple organizations along with well-planned experiments and measurements to evaluate the spillover effect.
- The choice of materials, protocols, and the team assembly are all good.
- Strengths of this project include the mix of adherents and doubters, the spectrographic data and H_2 capacity measurements, and the calibration of capacity results from all laboratories beforehand.
- This project's capable scientists are an area of strength.
- This project features competently performed sorption measurements that are reproducible, accurate, and precise.

Project weaknesses:

- It is not clear when a final conclusion will be drawn for the potential of spillover to meet the H_2 storage target.
- An area of weakness is how the project team just talks about "enhancement" values without discussing approximately where these values need to be for spillover materials to be useful.
- It is not clear that the theory behind H_2 spillover will be as uncontestable as the experiments.
- Analysis of the samples with a high reported weight percent is missing. The concern is that no conclusion may be reached on the optimum amount of H_2 that could be stored via spillover.
- A weakness of this project is its ill-defined future research and development plans. There is also a lack of go/no-go criteria, and it is unclear what the targets are. Achieving an additional 15% enhancement of a very small capacity number is a questionable metric.

Recommendations for additions/deletions to project scope:

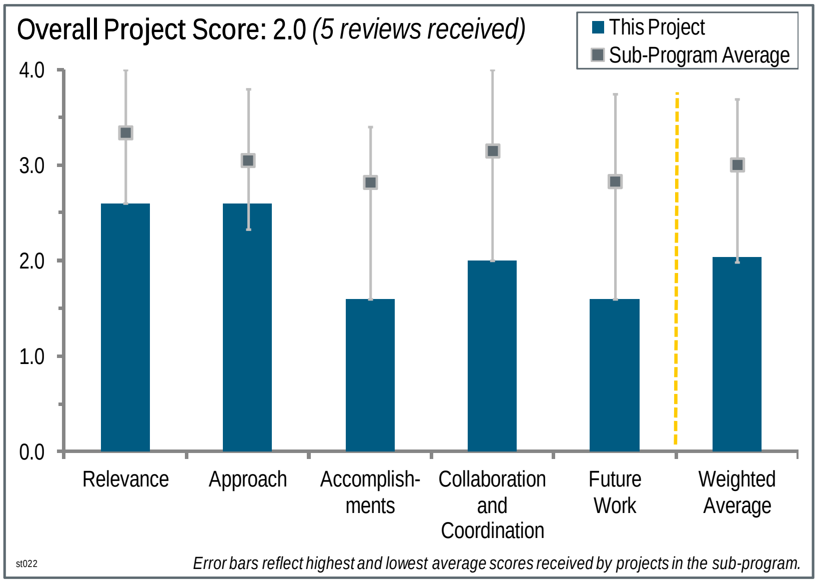
- It will be good for the PI to compile a table with the direct comparison of micropore/total pore volume changes among all of the samples with and without metal and with and without metal reduction treatment. This will help to draw an insightful technical conclusion for the cause of improved H_2 uptake of spillover samples.
- Other institutions within the Hydrogen Storage sub-program are also conducting related work. It is recommended to consolidate these projects or have clear distinctions between them.
- The project team should quickly develop a set of go/no-go criteria for this and other H_2 spillover projects. This could also encompass the “metal modified” metal-organic framework projects that have many of the same issues.

Project # ST-022: A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs for On-Board Vehicular Hydrogen Storage

Omar Yaghi; University of California, Los Angeles

Brief Summary of Project:

The overall objective of this project is to develop new materials to meet U.S. Department of Energy (DOE) system hydrogen (H_2) storage targets. This objective involves: (1) making a theoretical prediction of H_2 storage capacities to guide chemistry, (2) synthesizing lightweight crystalline porous solids for the metalation, and (3) measuring H_2 uptake and adsorption enthalpy. Covalent organic frameworks (COFs) for lightweight crystalline porous solids will demonstrate control of structure, topology, and interpenetration; consist of lightweight materials; be designed for functionality; and be suitable for metal impregnation.



Question 1: Relevance to overall DOE objectives

This project was rated **2.6** for its relevance to DOE objectives.

- This is an important project that examines possible new avenues to design room-temperature adsorbents for H_2 storage.
- The scope of this project is aligned with the DOE Hydrogen and Fuel Cells Program (the Program). Sorbent-based H_2 storage technology is one of the most attractive options for advanced storage systems. COF has certain advantages compared to carbon and metal-organic frameworks.
- Increasing the binding energy of adsorbed H_2 is critical for this technology in terms of the DOE goals.
- The relevance of the project as presented is important; for example, to improve binding energies and synthetic scale-up. However, the data presented did not seem relevant to establishing a pathway to achieve DOE project goals.
- This collaboration appears to be an effort at predicting structures of potential interest for storage applications. While some effort appears to have gone into computational design aspects of COF structures, it appears that little work has been accomplished over the past year in structures that have been synthesized. Rather, the empirical effort seems to be that of producing as many structures as possible while providing little physical insight from the less-than-optimized materials that have been made. While at the start of the presentation reference was made in a number of viewgraphs that illustrated data from several years, no apparent progress has been made since then in showing better material properties. While this is not a problem per se, it is not clear whether any attempt has been made at trying to optimize any of the new materials that have been synthesized over the past year.

Question 2: Approach to performing the work

This project was rated **2.6** for its approach.

- The theory-guided experimental approach should provide a quick evaluation of the potential of this class of sorbent.
- The approach is original but risky; some of the experimental results on synthesized and seemingly difficult-to-activate materials are far below theoretical predictions.

- It is unclear whether there is an attempt to address barriers in this work. The overabundance of previously reported work that was presented as part of the overview serves to highlight the lack of progress made over the past year.
- The theoretical approach is relevant and individually marks as a 3. However, the poor contributions and approach from the experimental side are disappointing.
- A description of the theory and methodology to compare simulation results with experiments should be provided. The agreement between theory and experiment is usually very good. It is unclear if the experimental data is rescaled by the specific surface, and whether the specific surface of the materials has been evaluated numerically either through an insertion method or a simulated BET measurement. It is also unclear how theory and experiments compare from the point of view of the specific surfaces and pore volumes, and how those are measured. In some cases it seems that the theoretical and experimental excess isotherms are closer than the absolute adsorption isotherms (for example, all of the materials compared in slide 5 of the PowerPoint presentation), and it is unclear whether there is an explanation for this.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **1.6** for its accomplishments and progress.

- The project has made very little progress toward metalation since last year. From the results, it can be clearly seen that the developed material will be far short of meeting the DOE goals.
- It is unclear if it will be possible to synthesize the promising material presented by the theory group, and if this material is practical. It is also unclear if it can be improved so that the systems' criteria are met at room temperature.
- Slide 21 shows a summary of the work as it pertains to the Program for the past year. Apparently the empirical effort consists of having produced one material, COF-320, for which a relatively low surface area of 1,620 m^2/gm and a 0.6 wt.% uptake at 1 bar and 77 K were measured. While slide 19 shows that this material can be synthesized to >10 gm levels, there is nothing to indicate in the data produced so far that such quantities at such surface areas are of topical interest to the goals of the Program.
- There is a lack of follow-up experimental work after a good structure is predicted. For example, COF-105 and COF-108 have never been experimentally made in reasonable quantity for the evaluation of their real H_2 storage properties. It is also not clear why COF-3xx samples were studied in depth. With such a small amount of H_2 uptake, it is unclear if there is a chance for this class of materials to ever meet the H_2 storage targets.
- There was only one slide presenting new data. Most of the work appeared to be focused on the production of gram quantities of linker molecules, showing neither pathways nor results of improved batch synthesis. This seems like a gross deviation from the tasks and milestones as outlined. It was disappointing that data from 2006 and 2008 were the major focus of the presentation and that all other results (slides 21 and 22) were in progress or not attempted yet. Based on the results presented, funding of the project should be discontinued; it appears that there is no concerted effort to finish tasks.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.0** for its collaboration and coordination.

- The collaboration between the theory group and the experimental group should be described in more detail.
- It appears that collaboration between the two main partners of the project is minimal.
- This collaboration does not appear to work too effectively, given the productivity of the empirical effort. Based on the presenter's inability to answer several of the questions posed, there appears to be a lack of engagement with the work that has been accomplished.
- The interaction between this project and other DOE Hydrogen Sorption Center of Excellence and Hydrogen Storage Engineering Center of Excellence partners is not clearly demonstrated. The experimental measurement should be validated at the National Renewable Energy Laboratory or another DOE partner facility.

Question 5: Proposed future work

This project was rated **1.6** for its proposed future work.

- There was no apparent path forward presented. It does not seem that this project is a priority of the principal investigators.
- It is not clear how the planned future work will ever address the current gap between where the project stands in COFs and the H_2 storage target.
- Results show enhanced storage capacity at room temperature; however, it is far below that of currently available technologies.
- Given the lack of accomplishment over the past year in having performed one measurement on one non-optimized material, the characterization work described as “work to be performed” should have been accomplished already.
- The authors have a path forward with a new material that could show real progress toward achieving some of the DOE goals. The best materials predicted by the theory group still would fall short of the systems DOE targets. It is unclear if there is a strategy to go beyond this material.

Project strengths:

- The project features good material synthesis capabilities.
- The effort put in by the theoreticians is a strength of this project.
- The project has improved understanding of the mechanisms. The theory team has proposed a new material.
- The theory-guided experimental approach could provide a quick evaluation of the COFs’ potential and compare their advantages and disadvantages to other sorbent materials.

Project weaknesses:

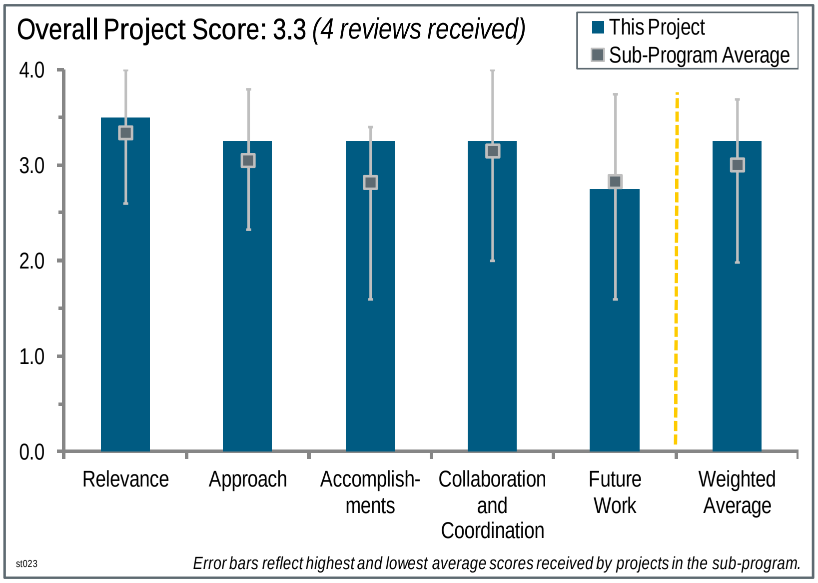
- This project’s empirical effort in addressing the goals of the Program has not been productive.
- This project is not making progress in terms of practical onboard H_2 storage applications.
- There does not seem to be any defined path forward to accomplish the milestones.
- No materials presented in the review so far have shown significant progress toward reaching storage densities in the ballpark of the DOE goals at room temperature.
- Although a lot of good theory prediction is coming out of this work, there is a lack of experimental follow-up on the good structures that have the potential to meet the target. It is also not clear why a lot of effort was focused on the materials with low H_2 which will never meet the target.

Recommendations for additions/deletions to project scope:

- It would be good to have a table of the properties of the materials examined by the group so far to better evaluate progress; for example, specific surface, pore volume, excess density adsorbed at 77 K and 298 K, and isosteric heat of adsorption.
- If the project team does not reach its milestones in September, the project should be discontinued.

Project # ST-023: New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randy Snurr; Northwestern University



Brief Summary of Project:

The overall objective of this project is to develop new materials to meet U.S. Department of Energy (DOE) volumetric and gravimetric targets for hydrogen (H_2) storage. The goal is to use metal-organic frameworks (MOFs) and polymer-organic frameworks (POFs) to create room-temperature H_2 storage sorbents that have both high heats of adsorption and large surface areas. This year's objectives specifically focus on: (1) obtaining validation for previous results; (2) developing high-surface-area materials for cryogenic storage and high-surface-area materials containing functional groups that can bind H_2 at room temperature; and (3) using modeling to screen cations and cation environments for their ability to bind H_2 and the resulting storage capacities, and to assess the relationship between high surface area, pore size, and strong binding sites with respect to performance.

Question 1: Relevance to overall DOE objectives

This project was rated **3.5** for its relevance to DOE objectives.

- This project is highly relevant to the DOE Hydrogen and Fuel Cells Program (the Program) in terms of the use of computational screening to help in the discovery of higher-capacity materials and providing new methods for increasing the adsorption enthalpies of physisorption materials.
- The principal investigators (PIs) in this collaborative effort have a clear understanding of the scientific issues and appear to work well together in addressing the thermodynamic and density issues associated with solving the storage problem. Both the theoretical and empirical efforts are focused efforts and include a "global" computational screening approach to addressing both the prospective gravimetric and volumetric requirements of the Program.
- Understanding the basic interaction of H_2 with complicated chemical functional groups and exposed metal centers in MOFs is a developing science, and this work contributes significantly to this effort. Ultimately, it needs to be known what materials are potential candidates for high-capacity, room-temperature storage, and the combined MOF/POF and calculation approach here is reasonable, even if the work is only partially successful at this point (e.g., high surface areas in MOFs, modification of the isosteric heat of adsorption [Q_{st}], and screening calculation development).
- The project, if successful, will have an impact on DOE storage objectives. However, it did not deserve an "outstanding" rating because while the science/scope is excellent, one cannot be certain that the framework materials will be applicable to transportation applications due to issues with purity and stability. However, they are a significant improvement over several of the hydride materials.

Question 2: Approach to performing the work

This project was rated **3.3** for its approach.

- The combination of approaches between calculation and synthesis is potentially the best approach to reaching DOE goals for this class of materials.
- The approach of combining the modeling and experimental work to develop new materials is a strength of this project.
- Through the combination and actual interaction of the synthetic scientists and the theorists, the project team has outlined an exceptional pathway to achieve its goals in this project. While not truly an inverse design approach, it is unique in that it addresses and limits the no-go synthetic possibilities.
- As with all efforts that have an experimental component, full materials optimization has not yet been achieved, at least in the case of the compelling manganese (Mn) POP materials. Approaches that minimize the extent of trapped solvent in structures of this type are critical in judging the potential for use of a material of this type for engineering applications. Supercritical CO_2, which is the approach that has been adopted post synthesis, has helped to address some of this problem. Perhaps an approach similar to Jeff Long's optimization of MOF-5 relying on synthesis in an inert atmosphere might also be worth exploring.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.3** for its accomplishments and progress.

- Progress has slowed since the prior year in terms of improved results, but not in terms of effort toward discovery, testing, and development of new materials. The project has shown a high level of effort in making progress toward DOE goals.
- From the standpoint of addressing the issue of heats of adsorption, the work on the low-surface-area Mn POP that shows a fairly constant enthalpy (ΔH) is of particular interest because it appears to be the only candidate system that displays such behavior, albeit over a somewhat short range of uptake. While it may fall somewhat out of the purview of the goals of this project, providing some level of physical insight into how such constant ΔH has been observed would be of overall scientific and technological interest.
- While the researchers have made excellent progress on their project, especially on the theoretical initiative, there is an issue with their "normalization" of the National Renewable Energy Laboratory (NREL) generated data to reach their milestone. The normalization factor applied is not valid. Also, it leads one to believe that their volumetric measurements are more in question, through their own admission. While good progress has been made on the purification and removal of solvents from the framework materials, there are limitations in that they cannot purify a material on-site at NREL to the same level as in their own laboratory. Granted, they are suffering from the history of erroneous results in the storage community at large, but their "correction" factor only exacerbates the problem.
- This past year does not seem to have yielded many experiments or results. Last year, there were indications that the researchers have characterization beyond the laboratory (neutron scattering), but no information was presented in this report. Speculation about the interactions of H_2 with theoretical or model structures is fine, but the real experiments and difficulties associated with activation and recycling are absent. The real gap is (not only in this project) between theory and experiment; multiple H_2 binding in first-row transition metals and light metals has not been shown in any of these systems (either structurally or spectroscopically), and indications are that the H_2 takes up significant volume next to its adsorption site, even with relatively high binding strengths (neutron diffraction). Most of the new experimental work seems to be through collaboration with NREL, and the data show significant discrepancies with Northwestern University's (NWU's) own measurements. Potential explanations were given, but applying a universal scaling factor to account for the difference between facilities is not reasonable and validates a lower value than indicated last year (albeit still a large value). Increasing Q_{st} seems to have had some mildly interesting results, but the data are only shown to 0.4 wt.%. It is certainly worthwhile to extend this measurement range to correlate Q_{st} and how it drops with coverage to metal content and species. The final uptakes on metal decorated systems will always run afoul of reducing specific surface areas with increasing metal content. The limits of this need to be understood for these systems.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The PIs in this effort appear to have a clear feedback approach that works within the NWU collaboration, and the help provided by NREL in the evaluation of their materials has had a positive impact on improving the analysis and synthesis of materials for this project.
- The technical validation through the collaboration with NREL is commendable. Other projects should do the same. Given that this project is nearing the end, the synthesis and modeling tools developed should either be continued or shared with the international community.
- NREL and the work with Parilla is the only evidence that there is interaction with other H_2 storage groups, and the corresponding results of this interaction were presented. This actually should benefit NWU significantly in improving its isotherm measurement capabilities for the future. It would be good to see some results from the project team's other collaborating interactions, but unfortunately there was little to judge in this presentation.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- Given the timeline, this is a reasonable effort, but it is unlikely to achieve DOE goals in the remaining period.
- The proposed future work is acceptable as long as the researchers get their sorption measurements issues resolved.
- There is a long list of future work with very little time remaining to accomplish the work. It is recommended that the remaining work focus on one or two goals only; specifically, those that will provide the ability to continue work in this area, such as validating the high-throughput computational screening and high-pressure measurements on one or two of the current best candidates for increased room-temperature capacities.
- While the PI has presented what seems to be a logical set of approaches for proposed work, he does recognize the limits of his first bullet point in the limitations of the use of metal additions in the attempt to increase the heat of adsorption, which will counterbalance the goal of high gravimetric density. Unfortunately, this overall avenue of pursuit in the interest of finding an MOF or POF (or generic coordination polymer) for H_2 storage applications may be too difficult a system to pursue, given issues such as precursor expense, solvent extraction difficulties, and limited charge transfer effects from the metal to linker (that might affect a reasonably constant ΔH). The low score in this case is not a reflection of the work as proposed by the investigators, but an assessment of the limitations of continuing to pursue this overall area of work for H_2 storage applications.

Project strengths:

- This project features unique synthetic approaches and an excellent group.
- This project features a strong collaborative effort with PIs who clearly understand the issues of the problem and have chosen a narrow, promising set of systems to investigate and optimize for the project.
- Strengths of this project include the combination of approaches, the expertise of PIs, its productivity, and the papers published.
- The collaboration with NREL to validate NU-100 H_2 storage properties was an important step and successful. Extensive synthesis and experimental characterization on the introduction of metals into the MOFs and POPs was another strength of this project. The development of high-throughput computational screening has the potential to dramatically reduce discovery and development time and efforts, and if proven successful through experimental validation, it will be of great benefit to the Program.

Project weaknesses:

- The volumetric measurements are an area of weakness.
- Extensive modeling and synthesis work has been accomplished, but it has resulted in only relatively minor improvements over prior materials.
- In the end, given what is now known about coordination polymers and their likely utility for storage applications, this overall avenue of research is proving to show its limits for technological adoption. While the PIs have

demonstrated a dedicated level of engagement in their work, the overall demands that combine ΔH, gravimetric, and volumetric targets will probably prove too challenging for materials of this type.
- Weaknesses include linking theory to experiment, and a lack of detail on the impacts of metal incorporation. There are unsatisfactory in-house isotherm capabilities and/or sample reproducibility between facilities, and weak external collaborations.

Recommendations for additions/deletions to project scope:

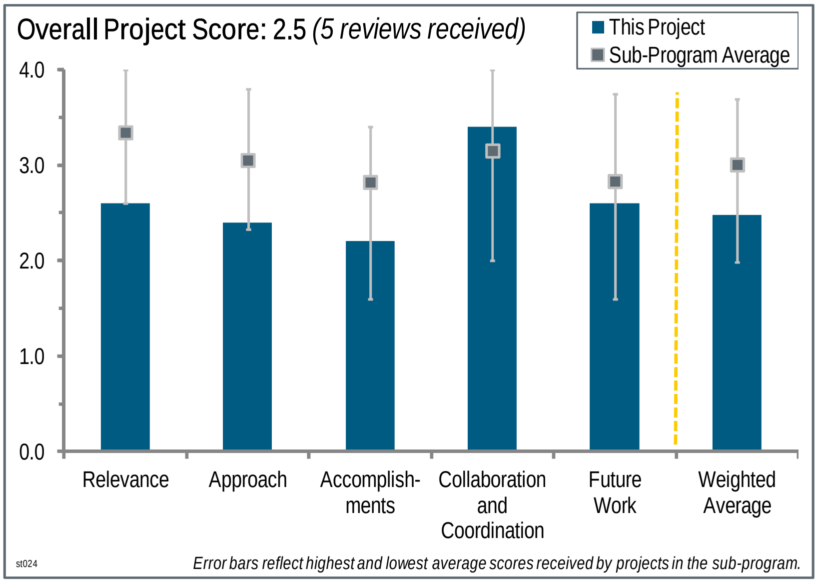
- The PIs have laid out the best course of action for their work and should continue to pursue their work as outlined in their presentation.
- The high-throughput computational screening is potentially a very powerful approach. However, it is very important that it is validated through experimental work before the end of the project. One suggestion would be to randomly select a few (feasible) candidate materials from the computational analysis (some with high predicted capacities and some with low capacities) and test these to see how well the computational models predict their H_2 storage properties. The calculated capacity plots do not identify specific materials; therefore, it is difficult to evaluate if there is a general trend that high gravimetric capacities correspond to low volumetric capacities. At a minimum, this potential correlation should be evaluated on the present data set.

Project # ST-024: Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

Angela Lueking; Pennsylvania State University

Brief Summary of Project:

The overarching objective of this project is to synthesize designer microporous metal-organic frameworks (MOFs) mixed with catalysts to enable hydrogen (H_2) spillover for H_2 storage at 300 K–400 K and under moderate pressures. This project addresses the barriers of gravimetric capacity, minimum and maximum delivery temperature, maximum delivery pressure from a tank, and volumetric capacity.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **2.6** for its relevance to DOE objectives.

- Room-temperature H_2 adsorption is a very attractive path, and spillover is critical to this path.
- The evaluation of whether spillover has any potential to be a viable method for room-temperature H_2 storage is relevant to DOE objectives.
- The project is focused on assisting DOE with unraveling the controversy and confusion surrounding the topic of spillover as applied to H_2 storage. The relevance is good; the principal investigator (PI) has performed a relevant experimental project using H_2 uptake and spectroscopic studies to provide reproducible data on the model spillover materials.
- The DOE Hydrogen and Fuel Cells Program (the Program) is concerned with the wide variability of spillover measurements, so it is clearly important to help out with the reproducibility, methods, etc. It is unclear why these efforts should supplant the original goals of this work, as there is already a group charged with this mission (National Renewable Energy Laboratory [NREL]). In addition, although it is important to find measurements that prove/disprove this concept, it is unclear what the goal is regarding enhancement. It is unclear what value or range of valves (enhancement) constitutes success, or at least indicates that this concept might (eventually) yield materials to meet DOE targets.
- The spillover effect is in question as a meaningful method for H_2 sorption. It is important to understand, but at the present it does not seem likely to be a viable mechanism. In addition, there is a larger and more focused project that will likely go well beyond this one, making this project less important. Working at 20 bar may provide data that is valid at those conditions, but that is not where the DOE Office of Energy Efficiency and Renewable Energy (EERE) is aiming. High pressure for room-temperature adsorption is needed to reach DOE goals, so in that aspect the work is not fully aligned. This really would fit better in the DOE Basic Energy Sciences (BES) Program or the National Science Foundation.

Question 2: Approach to performing the work

This project was rated **2.4** for its approach.

- Accurate measurement is critical to the success of this project. The PI deserves all of the credit for modifying the original approach in order to address the reproducibility issues.
- The approach is sound. Getting reproducible results is important, even though it has proved difficult. It is meritorious that the group changed direction when it was the right thing to do. On the other hand, doing lots of

work at only 20 bar and room temperature is not investigating the really important adsorption area and risks missing the real impact for the EERE goals.

- There are several approach slides suggesting a fluxional scope. In the original approach, it is desired to maximize metal dispersion (it is unclear how that will be measured) and optimize H_2 receptors. It is unclear what is meant by “optimizing H_2 receptors.” Then, there is a search for correlations between spillover and functional groups. It is unclear how the proposed experiments will put bounds on the potential of spillover to meet automotive applications.
- Prior work focused on improving the quality of the measurements and validation. The focus of the 2012 work is less clear. It appears that more questions have been generated than answers regarding key material performance behavior.
- The PI’s approach is to validate (or not) historic observations of the controversial and often irreproducible phenomenon of storing a small excess amount of hydrogen on surfaces via the well-known (to catalyst scientists) spillover of hydrogen onto substrates. The PI was careful to explain that the research was directed at validating (or not) spillover on known materials types and developing some potential mechanistic information, not developing new materials for storage via spillover. The PI used a variety of appropriate spectroscopic techniques correlated with H_2 sorption studies at room temperature and at relevant pressures that were validated by NREL. This approach is good, and as the PI recognizes, it is fraught with difficulties because searching for a potential minority species responsible for the very small (0.1%) amount of spiltover hydrogen stored on substrates at room temperature is a difficult task.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.2** for its accomplishments and progress.

- The project team has made good progress in collecting spillover evidence. However, it is not clear how the base materials were chosen for the study because the MOFs CuBTC and IRMOF-8 have low capacity.
- Results from collaborators’ work were shown, but it was not clear whether much progress has been made by the PI. No high-pressure results were presented. Very few new material results were presented. Many questions about the H_2 storage performance of current materials that should be easy to address have not been answered by the current experimental work.
- Progress has been slow, which may reflect the fragility of the underling concept. It is unfortunate that the H_2 signal is so poor in the Temperature Programmed Desorption, because it makes the H_2 uptake and the nature of it unclear. The effect of oxygen is interesting, but it is hard to tell if it is meaningful in storage because the majority of the gain is below 1 bar. Indeed, it may be hurting the usable amount because the slope with pressure seems lower.
- On slide 15, the data indicate approximately 0.5 wt.% H_2 storage capacity, yet the notes indicate an irreversible reaction. It is unclear how this is evidence of spillover, and the implied reversible concept. Perhaps this is not hydrogenation. Concerning slide 17, it is unclear why the C=O infrared absorptions would occur in nearly the same place when a metal is still coordinated to the putative COOH functionality. It is not clear if the PI (or the literature) has model complexes that show similar hydrogen uptake that support the project’s assertion. If this hydrogenation has occurred, it would be interesting to know what storage capacity the material has. In reference to slide 21, it is unclear if the pores are sufficiently large to allow “infiltration” of $PtCl_6^{2-}$ anions. If the PI chooses MOFs that have little or no preference for the metals the researchers are doping, it is unclear if the MOF structure will stay intact. It is also not clear how one can measure the degree of infiltration. It is understood that only a portion of the funding was acquired this fiscal year.
- The approach was carried out carefully, and the results were reproducible and the sorption experiments were validated by NREL. One can have high confidence that the results shown are relevant to answering some of the questions about the mechanism(s) of storage of small amounts of H_2 by spillover on surfaces, and have the potential to lead to some understanding of the chemical and physical limits of this storage approach. If there is a criticism to be made, it could be that the techniques used developed qualitative data. With a substantial amount of additional work, some of this could have been made semiquantitative and might have enabled a slightly more compelling story regarding the potential of the relative concentrations of the absorbed species. As such is typically the case in such studies, this would be very difficult, but it would add tremendous value if more quantitative spectroscopic analyses were available.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- A good team of collaborators has been assembled and this work is being leveraged with a present BES project.
- The PI demonstrated good effort in collaborating with other groups to address the reproducibility issues, both in measurement and materials synthesis.
- This project features good collaboration with NREL and others, as well as positive interaction and coordination with a BES-funded project.
- There is good collaboration with the NREL-led spillover validation effort.
- Collaborations are appropriate and the coordination, especially with NREL, was apparent.

Question 5: Proposed future work

This project was rated **2.6** for its proposed future work.

- Changing the isotherm shape is well worth pursuing.
- The project team should plan to make the doping methods more in line with the project goals. The value of the other proposed future work to the project and the Program is unclear.
- The planned work may result in further fundamental understanding. However, with the current understanding that spillover will not meet the DOE 2017 target of 5.5 wt.% H_2 system capacity, the PI should deliver a plan to address this issue.
- Plans for future work were fine, but in the very near future the researchers will be focused on meeting the go/no-go decision metric of demonstrating a 5.5 wt.% material. Given their current results and the comments the PI made, it seems unlikely that this criterion will be able to be met via spillover. This is not a criticism of the PI; this is just what the physics and chemistry appear to allow.

Project strengths:

- Strengths of this project include the coordinated effort in understanding the real spillover effect and experimental reproducibility.
- Substantial rigor is applied to the experiments undertaken.
- This project features good collaboration with NREL.
- One strength is how the researchers are looking at a mechanism and not making a better material, per se.
- The project team has competently carried out experiments that are reproducible, with validation from others.

Project weaknesses:

- Compared to the best baseline materials, it is not clear how much of the gap the spillover can address in order to achieve 5.5 wt.% excess H_2.
- It is unclear how this project will generate new materials that have a path to meet DOE targets. Although exploring spillover is of fundamental (BES) interest, without bounding the potential (perhaps with theory) of the proposed materials, it is difficult to conclude any progress has been made.
- It is unclear whether the few materials tested have any significant improvement in reversible room-temperature H_2 storage.
- The project has become a little unfocused over time, and the area is largely covered by other projects.
- In the approach, perhaps more emphasis should be placed on obtaining semiquantitative information on species adsorbed. Researchers could possibly look at other indirect methods to quantify hydrogen spillover; for example, via a chemical reaction to “trap” adsorbed hydrogen deuteride (HD), with potentially more chance of quantifying the chemically trapped HD. DOE is expending a significant amount of resources chasing down what appears to be a very minor probability of achieving anything more than a minor amount of H_2 stored. This is not a criticism of the PI’s effort, only a comment about the reality of practical H_2 storage via spillover.

Recommendations for additions/deletions to project scope:

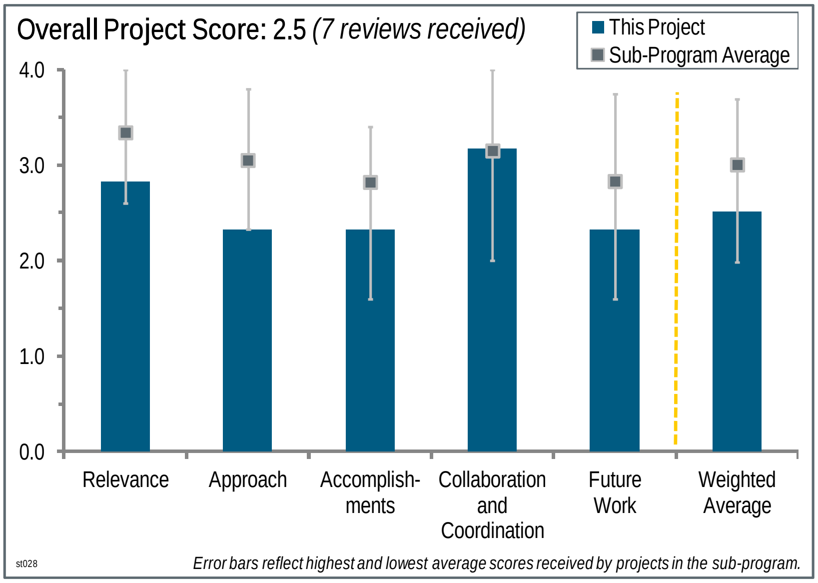
- The PI could consider some material-level calculations based on the current available experimental data and recommend what kind of the material properties one should achieve in order to meet the system target of 5.5 wt.% H_2 with this spillover approach.
- The work done would be more highly valued by BES, and it would be wise if it were possible to hand this contract to BES at the go/no-go point. While this reviewer knows of no examples of this type of action, it would be best for all programs and the PI.
- The project team should develop a chemically viable "vision" of what the ultimate spillover mechanism would allow for with regard to the capacities, temperatures, and rates of H_2 release from the ultimate spillover material.
- No significant improvements in the verifiable ability of the materials being evaluated to be used as a practical means of onboard H_2 storage have been demonstrated. Given that the May 2012 go/no-go criteria have not been met, it is recommended that work on this project be stopped.

Project # ST-028: Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

Christopher Wolverton; Northwestern University

Brief Summary of Project:

This project aims to address the barriers of system weight and volume, charging and discharging rates, and the lack of understanding of hydrogen (H_2) physisorption and chemisorption by combining materials from distinct categories to form novel multicomponent reactions. Systems studied include complex hydrides and chemical H_2 storage material mixtures, as well as novel multicomponent complex hydride materials and reactions. The study's approach blends H_2 storage measurement and characterization, state-of-the-art computational modeling, detailed catalysis experiments, and in-depth automotive perspectives.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **2.8** for its relevance to DOE objectives.

- The goal is to design novel metal hydride materials using composites of materials.
- This is a fundamental effort that aims to understand reaction pathways and composite principles, yet it clearly considers DOE targets such as weight, volume, and impurities in the output H_2.
- This work is aimed at probing the effectiveness of combining theoretical predictions of complex hydride reactions with experimental work. The experimental effort appears to be the bottleneck in this effort. Two particular systems for study had been identified in 2011: magnesium borohydride ($Mg[BH_4]_2$) combined with lithium borohydride ($LiBH_4$) and the $Mg(BH_4)_2$ combined with magnesium amide ($Mg[NH_2]_2$). Theoretically, these systems appear to make some headway toward the DOE Hydrogen and Fuel Cells Program (the Program) goals.
- This joint project of Northwestern University (NWU); the University of California, Los Angeles (UCLA); and Ford Motor Company involves the prediction and demonstration of mixed component sodium-magnesium-boron-nitrogen (Na-Mg-B-N) hydrides with storage capacities that are potentially large enough so that the DOE targets for passenger vehicles might be met. Experiments are being used to determine the as-prepared and decomposition phases in order to ascertain reaction pathways. The team is also looking at catalysts to enhance the kinetics (apparently, only desorption so far with very limit reversibility being shown) and theoretically identify the mechanisms that control the kinetics. The team's objectives generally comply with the DOE targets and goals.
- The project is focused on addressing key barriers with a variety of high-capacity hydrides and is aligned with the DOE objectives. The first item listed under "Barriers to address" is the "Lack of understanding...," which seems more appropriate for a DOE Basic Energy Sciences Program project. It would be better to focus on a clear objective (e.g., kinetics, reversibility) rather than just the lack of understanding. The lack of understanding clearly needs to be addressed, but the goal should be improvements in the material, not just a better understanding.
- The H_2 sorption properties of multicomponent mixtures of complex hydrides are being investigated in this project. Although the project is providing some new understanding on H_2 reactions in mixed hydride systems, the technical barriers encountered in these systems, most notably slow kinetics and poor reversibility, have severely

limited their applicability for onboard storage applications. Although the initial idea seemed promising, the limited success in meeting DOE storage material goals is minimizing the relevance of the project.

Question 2: Approach to performing the work

This project was rated **2.3** for its approach.

- This project systematically considers fundamental reaction pathways with mixtures and composite hydride materials. There is an unusually good combination of theory (calculation) and experimentation. Although this project should not necessarily be expected to result in a new material that would meet DOE targets, it will provide some useful basic understandings.
- As with a number of other projects that relate to destabilization reactions, the x-ray diffraction (XRD) work used to assess reaction product phases provides a limited amount of information. Other analytical techniques need to be pursued to identify the phases that have been formed. A clearer comparison of the results of adding a cobalt (Co) catalyst to the $LiBH_4$-containing system would be of use, especially if in the Co-containing case, diborane (B_2H_6) production is not observed. The activated carbon (AC) addition to pure $LiBH_4$ has been done before by Vajo at HRL Laboratories, with similar observations. The overall goals of the $LiBH_4$ work are not entirely clear. The reviewer wonders if the plan is to look into the reversibility of this material.
- The approach being used to discover improved H_2 storage materials is a combination of state-of-the-art first-principles calculations (NWU and UCLA) of possible hydrides and their structures along with predicted reaction pathways. More emphasis is now on the role of defects in diffusion processes with implications for better understanding of the kinetics. Conventional volumetric measurements of storage capacities and kinetics are performed at Ford and NWU, where the latter's researchers are mainly looking for more effective catalysts. While these materials are characterized by XRD and infrared (IR) spectroscopy, other more insightful techniques (e.g., Nuclear Magnetic Resonance [NMR], Raman, and neutron scattering) could be very useful to identify reactants and products more completely, especially with many systems that are amorphous and/or highly disordered. The last point was strongly recommended at the 2011 review as well, but it was not pursued.
- The general approach, as presented, seems to be effective, with computational predictions of reactions guiding the experimental efforts. However, there are a number of key problems with these materials that are not being clearly addressed: (1) decomposition temperatures are too high, (2) formation of stable intermediates limits reversibility, (3) slow kinetics. This project should have a clear focus on these barriers.
- An experimental and computational approach is being used to predict novel materials and reaction pathways, to synthesize and characterize the best candidate materials, and to improve H_2 sorption kinetics by catalysis. Unfortunately, the technical effort has not been placed in the larger context of the considerable work that has already been performed by other investigators in this area. If the principal investigator (PI) and his team had built upon that work more effectively, they would have avoided unnecessary duplication, thereby facilitating a more streamlined and focused approach. It is critical for the project team to clearly identify the remaining technical barriers and then provide a detailed plan on how those obstacles will be addressed.
- The project's approach did not acknowledge the long and well-studied history of this general approach. The existing literature in this area seems to have been disregarded. It seems the presenter is not an expert in the techniques of characterization of these complex, often amorphous materials, and was unfamiliar with basic requirements of H_2 release experiments using (partially) reversible materials. The presenter seemed unfamiliar with the chemistry of the boranes and of the metal borohydrides. The project did not incorporate an approach to address feedback given last year on characterization issues. The presenter was unfamiliar with DOE targets and their implications (materials versus system requirements).

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.3** for its accomplishments and progress.

- The experimental effort seems to be making some progress with the ammonia-containing systems. Overall, an effort aimed at looking at the ultimate lower temperature limits of solid-state diffusion (a difficult problem) might help to illuminate the overall effectiveness of using reactions of the type described in this work, and at least give appropriate temperature ranges for these reactions (which are very high from the standpoint of Program goals).

- A significant amount of good work has been accomplished and substantial understanding has been developed. Eliminations of unpromising materials have been logically made. From a truly practical perspective, statements such as "ammonia release is practically undetectable" are not very convincing. Discussions on the subject of impurity detection limits with the PI's equipment and optimum test techniques were unsatisfactory. There seems to be growing doubts that these particular materials will ever have adequate properties to allow vehicular application.
- More meaningful progress might have been made had the PI been more familiar with previous published work in this area. Proposed diffusion of BH_3 through BH_4^- solid indicated a lack of understanding of borane chemistry, which is a prerequisite to working effectively in this area. H_2 release experiments on a (partially) reversible system were performed against a vacuum, rather than against H_2 back-pressure. There were not enough cycles on the (partially) reversible system to demonstrate even partial reversibility. The PI did not know the prior literature on $B_{12}H_{12}^{2-}$ anion chemistry with respect to H_2 storage mechanisms.
- Some potentially attractive candidate reactions have been theoretically predicted (e.g., those involving $Mg(B_3H_6)_2$ and AlB_4H_{11} phases) that were at least partially verified by testing or other analyses, but none exhibit the highly desirable reversibility behavior at moderate conditions. The work on the $LiBH_4$-$Mg(BH_4)_2$ phases appears to show much of the same behavior as found and published by other research groups over the past couple of years. While the Co-AC catalyst does give some improvement in the desorption properties of various borohydrides, the impact is about the same as already noted by others using a variety of catalysts and additives. No systematic assessments have been done, nor do any novel insights seem obvious from the present results.
- A significant fraction of the technical effort in 2011/2012 was devoted to improving the sorption kinetics and reversibility of selected mixed hydride systems. Although minor improvements in dehydrogenation kinetics were observed in the borohydride and amide systems, the sorption rates and reversibility remained far below the limits of acceptability for practical storage applications. There are several specific concerns: (1) the role played by $B_{12}H_{12}^{2-}$ in the sorption reactions in the borohydride/amide systems must be clarified in more detail—a more complete characterization (especially NMR analysis) is needed to elucidate the role of $B_{12}H_{12}^{2-}$ in the sorption mechanism; (2) the path forward for significantly improving the kinetics remains problematic—a solid plan to overcome this barrier is lacking; and (3) poor reversibility is apparent in all systems—the reasons for limited reversibility have not been fully articulated, and a detailed plan to overcome this obstacle has not been provided.
- There are a number of deficiencies with the experimental work. First, it is not at all clear what the reaction pathways are. An accurate description of the pathways is necessary to inform the computational work and ultimately refine the material in some way. The appropriate characterization techniques (XRD + NMR + ...) need to be performed to determine exactly what phases are formed during decomposition and, similarly, what phases are formed upon re-hydrogenation. Second, experimental measurements need to be made to determine the thermodynamics of the reaction. From the results shown the temperatures are very high, and it is not clear how they will be reduced. It is proposed that $B_{12}H_{12}^{2-}$ is an intermediate, but others have clearly shown that this is a very stable compound that is an end state, not an intermediate. If $B_{12}H_{12}^{2-}$ is an irreversible side product (as opposed to an intermediate), it would suggest that other reaction pathways are taking place other than those used in the modeling. In this case, the predicted thermodynamic values would not apply. The work on $LiBH_4$ does not seem logical. This compound has an equilibrium pressure of 1 bar at approximately 400°C—new catalysts are not going to reduce the equilibrium temperature.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- This project is an excellent example of good collaboration.
- The collaboration with Ozolins works particularly well.
- It appears that there are a number of nice collaborations with other researchers, but it is not really clear how they all fit in and what they did.
- Collaborations with multiple university, government laboratory, and industrial laboratory partners have reinforced and augmented the total technical effort. A strong collaboration with an expert in solid-state NMR would be an important addition.
- Excellent interaction was indicated between the theoretical members of this team and also with some experimental groups on some complex hydrides such as Mg-BH_4-NH_2 and AlB_4H_{11}. There seems to have been limited collaboration concerning catalyst work on the Co-AC catalyst with the $LiBH_4$-$Mg(BH_4)_2$ system.

- The lack of knowledge on the current literature indicates that there is limited collaboration.

Question 5: Proposed future work

This project was rated **2.3** for its proposed future work.

- Given the nature of the project, the proposed work makes sense. The computational effort directed at mass transport would be of particular value.
- The proposed future work is good, but the researchers should extend their work into compositions that might offer more immediate hope.
- It is a very good idea to stop work on the borohydride/amide mixtures, because they are not promising. Experimental verification of proposed reactions of $(NH_4)_2B_{12}H_{16}$ and related phases may be useful, providing appropriate methods that are used for characterization. Also, extending and expanding the first-principles calculation of the roles of defects and diffusion processes on reaction kinetics could be very productive because the intrinsic kinetics appear to be rate limiting for reactions of the alanates and borohydrides. However, there does not seem to be any vision or focus regarding future experimental efforts on catalysts with complex hydrides or developing systems with better reversibility.
- There are a number of weaknesses with the proposed future work. It is not clear what is going to be done to reduce the equilibrium pressure. Simply stating "optimize reversibility conditions" is not sufficient—it would be good to know exactly how this will be done. The computational effort has predicted a number of promising multicomponent hydrides, but there is a clear disconnect with the experimental work. The actual reactions that are occurring are not the ones predicted. It is not clear if there is any plan on how to deal with stable (irreversible) side products that limit the reversible capacity.
- The future plans provide insufficient detail to allow for an objective review. (For example, Future Plans, slide 23: "Optimize reversibility conditions for $5Mg(BH_4)_2$+$2LiBH_4$ mixture.") This provides no information about what will actually be done to "optimize reversibility." The same criticism holds for the future work on catalysis. Given the daunting challenges posed by prohibitively slow kinetics and poor reversibility in all of the systems that are being investigated, it is essential that a clearly stated and more detailed plan for addressing those problems is provided.

Project strengths:

- The computational work seems to be pretty good and has identified a number of interesting multicomponent hydrides.
- The project team is looking at reaction pathways in a good, fundamental sense, and trying to develop an understanding of catalysts.
- The initial idea of exploring multicomponent mixtures of complex hydrides was compelling. The research and development team comprises acknowledged experts in computation and modeling, catalysis, and materials characterization. The computation and simulation effort is especially impressive.
- The two theoretical groups at NWU and UCLA have developed very insightful and effective computation procedures and are performing the prediction and modeling of potential storage materials. A strong working relationship has been established between the theoretical and the industrial partner, Ford. However, the sense of direction for the effort is not clear because the original Ford co-PI left the project for another position.

Project weaknesses:

- For the empirical effort, there is some redundancy of previous work. More analytical techniques need to be employed for phase identification.
- The compositions presently being studied are not likely to have near-term vehicular application.
- Mostly H_2 desorption behavior was described from the experimental studies, where the investigated materials have limited reversibility. The large amount of additives needed to improve desorption kinetics is a concern, and a scheme to create a more fundamental approach is still lacking. Using primarily X-rays and IR to characterize these materials is insufficient, because often the most interesting species are amorphous. It is a very long reach for connecting first-principles calculations of defect formation and migration to establishing reaction pathways and kinetics.

- The experimental work seems weak. Little characterization work has been done to determine the actual reaction pathways. XRD is useful but insufficient; other techniques (e.g., NMR) are necessary to identify amorphous phases. There seems to be a disconnect between the computational work and the experimental work. There does not seem to be a clear pathway for making the necessary improvements.
- Only limited success has been achieved in identifying a candidate material that even approaches the DOE targets. A detailed plan for overcoming the serious obstacles of slow kinetics and lack of reversibility is not evident. The role of $B_{12}H_{12}^{2-}$ could be critical in the overall sorption reaction mechanism—a careful and definitive investigation should be conducted.

Recommendations for additions/deletions to project scope:

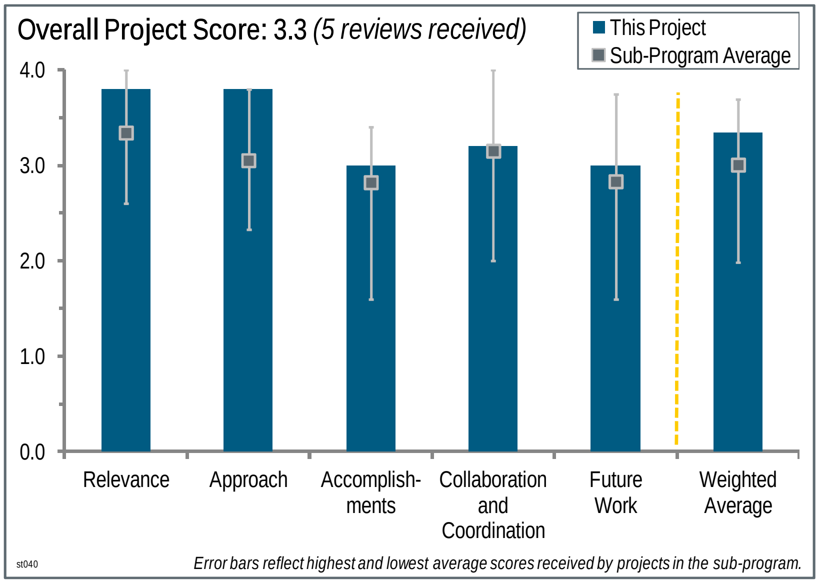
- During the question and answer session, there were strong suggestions to add NMR studies. Otherwise, the project team should continue development of fundamental understandings and begin thinking about more practical mixtures.
- A strong recommendation is that additional characterization techniques such as NMR and neutron scattering should be used to identify any promising materials and their reaction products. To have a more complete vision of the catalyst/additive, phases that exhibit both absorption and desorption should be investigated along with reducing the amount of these additives. The system $LiBH_4$-$Mg(BH_4)_2$ has been widely studied in the international research community and shows virtually no promise as a reversible H_2 storage candidate under moderate conditions. Hence, its role as a model system is doubtful. The team should focus the remainder of its project resources on alternative materials. Ideally, these hydrides would have greater reversibility than the borohydride and amide mixtures.
- There should be a feedback from the experimental studies back to the computational work because the predicted reaction pathways seem to be different than what is really going on. Better characterization is needed to understand these complex reactions.
- The results to date on this project do not provide a very compelling case for the adoption of these materials in reversible H_2 storage applications. The PI and the DOE Technology Development Manager should have a candid discussion about continuation of the project in view of the weak future plans for overcoming the existing technical obstacles. Specifically, a well-formulated NMR study should be included in the project. This should provide useful information about the role of rate-limiting intermediates such as $B_{12}H_{12}^{2-}$ in the overall mechanism.
- This reviewer recommends discontinuing the project.

Project # ST-040: Liquid Hydrogen Storage Materials

Benjamin Davis; Los Alamos National Laboratory

Brief Summary of Project:

The objectives of this project are to: (1) develop ammonia borane (AB) (approximately 15 wt.% usable hydrogen [H_2])/ionic liquid (IL) mixtures that have sufficient H_2 capacity, release kinetics, stability, and fluid phase properties; and (2) work with the Hydrogen Storage Engineering Center of Excellence (HSECoE) to ensure compatibility with system designs. To prevent or forestall the formation of insoluble products after extensive H_2 release from AB, the team will develop strategies to define usable temperatures and times as a guide for future designs.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.8** for its relevance to DOE objectives.

- This project is well aligned with the DOE objectives. The development of a high-capacity liquid carrier based on AB will likely meet many of the DOE targets.
- This project is oriented directly toward HSECoE needs for data on and improvements of AB to assess and develop practical vehicular systems. It is therefore directly related to DOE objectives and targets.
- A suitable liquid-phase carrier for AB slurries is very important to chemical H_2 storage systems for vehicular applications.
- The project is highly relevant to DOE objectives and supports the DOE Hydrogen and Fuel Cells Program well. Fluid chemical storage materials offer compelling advantages over solids (such as pure AB), so this is a valuable project. The project has good ties with the HSECoE, which helps to guide goals and maintain relevance.
- The goal is to develop a liquid-phase H_2 storage material using ILs. This is fully consistent with DOE goals in this area and is important to making AB a practical storage material. There are close interactions with the HSECoE. The relationship with the HSECoE started early on, so this project is now well connected and integrated with the HSECoE. The target of 5 wt.% is a little low. The cost focus is good. The optimization of AB fuel blends for use in ILs is a good idea.

Question 2: Approach to performing the work

This project was rated **3.8** for its approach.

- ILs have significant promise for use with AB. The project features good approaches of striving for simplified AB product structures and looking at a greater range of ILs.
- The approach to the project is sound—concentrating effort on two strategies to deliver materials with the desired properties. These strategies are based on reasonable scientific assumptions. With regard to specific formulations, it would be good to see a greater trend toward an understanding of core principles rather than what appears to be at the moment a trial-and-error approach.
- The overall approach is good. The integration with engineering and dealing with the cost up front is also good. The survey of the properties of AB in ILs is a good idea. The use of Boron Nuclear Magnetic Spectroscopy is a good idea, and the researchers have developed a good measurement method. There is an issue with how much H_2

is released at room temperature in the IL—it seems to be quite high. The work on minimizing impurities such as ammonia, borazine, and B_2H_6 is good. There is an issue with unidentified impurities, which can be way too high, based on the researchers' observations.
- This project is nicely focused on the key barriers for liquid carriers of this type: (1) keeping the solution/slurry in a liquid phase before and after hydrogenation and (2) finding the appropriate liquid to maximize capacity, rate, stability, etc.
- The principal objective is to develop AB in an IL form that will not precipitate solids during the onboard dehydrogenate reaction. This will greatly simplify the system. The work is designed to directly satisfy HSECoE needs. In addition to coming up with a stable liquid system, other important side considerations are being considered; for example, loss of effective H_2 capacity, stability, compatibility with regeneration, etc.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- Interesting ILs and additives to ILs that optimize the use of AB have been identified.
- A number of accomplishments were achieved this past year that address the key issues. The demonstration that a slurry, formed from AB and a hexyl-AB (6 wt.%), transforms into a liquid after dehydrogenation is an important achievement. The ability to keep the fuel in liquid (or slurry) form is critical, and this is a nice proof of concept. It is nice to see stability measurements are being performed during the screening stage. It would be useful to expand these to higher temperatures (i.e., above room temperature). The project team has made good progress overall. It must identify and deal with the impurities in a better way. The use of binary materials with AB is a good idea. More details on the properties of the pure mixtures without ILs would be good. The researchers have the measurement method under control. It would have been good to have seen more details on the new additive synthesis. The researchers are going to have to deal with how much H_2 is released at room temperature. An interesting and important result is the difference in solubility of polyborazylene in ILs.
- Good progress has been made in developing new ILs for the solution of AB. However, it is difficult to understand the trade-offs involved. How much of the excellent H_2 capacity of AB is lost by dilution in a stable IL version. It appears that the 40% AB levels required by the HSECoE have not been met thus far. A problem is the presentation of the results in mols H_2/g liquid, instead of simply wt.% H_2. Volume dilution effects do not seem to be covered. It would be useful to clearly show that the best products to date still have the potential to meet the DOE system targets when built into an HSECoE demonstration system.
- Some progress has clearly been made, but there remains a lot to do. The reviewers-only slides indicate that there have been several factors that may have impeded progress this year, and it is understood that this is a difficult and complex problem. Data from only one AB/IL/additive blend was presented and, although improved over the non-additive control, the amount of H_2 released before the phase change is a long way short of the targets. Recognizing the water content of ILs is an advance in one sense, but it has probably consumed appreciable resources and calls many of the previous results into question. However, everyone recognizes the need to avoid boron-oxygen bonds, so hopefully further progress will ensue from the new understanding of the raw materials. It is good to see quantitative data on the impurities from these systems, and this is progress in a sense, even if the borazine quantities in particularly are alarmingly high. It seems that the fluid environment may encourage borazine formation, and this is intuitively understandable when considering the need for three AB-derived units to align correctly in the ring (solid AB starts with all molecules aligned in a single direction). It is possible that the additives under consideration will counteract this problem by forming less volatile species; nevertheless, this is an issue the project team needs to watch closely and consider alternatives to AB if necessary.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- The collaborations are excellent. L. Sneddon of the University of Pennsylvania is transitioning to a consultant role. The project team is bringing on T. Baker from the University of Ottawa to deal with the catalysis issues. The team has excellent collaborations with the HSECoE.
- This project seems well integrated with the HSECoE, and there are a number of good external collaborations.
- It is unclear if there is any collaboration with the Pacific Northwest National Laboratory AB slurry project.

- There are a few useful collaborations in addition to the basic one with the HSECoE.
- The project has close ties with the HSECoE and is responsive to its needs. There have been extenuating circumstances with other collaborators, but those issues appear to be resolved. This PI should engage the university collaborators in selecting additives and ILs, respectively. The PI surely intends to do this anyway, but the importance of sound choices in these areas if the project is to make significant gains toward the targets must be stressed.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future work seems reasonable.
- The proposed future work is essentially a continuation of the current work, incorporating new formulations to synthesize and test. While this is reasonable, a new or more focused approach may be justified if purity or capacity (before phase change) characteristics remain substantially short of targets.
- Although not very detailed, the general directions for the future work seem to be adequate.
- It is good to see that the solubility survey will be complete in fiscal year (FY) 2012. A number of key studies are necessary to complete this milestone. It is a little less clear exactly what will be done in FY 2013.
- The idea of using a reproducible source of polyborazylene is good for making comparisons between different IL formulations; however, it becomes less valuable if the solubility characteristics are different from the "real" dehydrogenation product. The exact AB/R-AB mixture and the thermal conditions used to generate H_2 will probably have a major influence on the structure and solubility of the spent fuel. The team should ensure that it does not get sidetracked too far by considering the solubility of what may be an unrepresentative material.
- The researchers have a good plan on where to go. They will continue to interface with the HSECoE. They need to get back to getting H_2 release rates. They also need to deal with regeneration issues. They did not specify much on the catalysis that they will be doing. They need to deal with the impurity issues as well as the release of H_2 at room temperature.

Project strengths:

- This project is well aligned with DOE objectives and the work is sharply focused. Good progress has been made over the past year.
- The project team has significant expertise with AB and ILs.
- The project team has a good relationship with the HSECoE. The project team and collaborators are experts in this field.
- The researchers are making excellent progress on a good idea. The use of a liquid fuel system makes it more likely that some of the existing infrastructure can be used. There are close interactions with the HSECoE, and the project team is dealing with cost issues up front. The researchers have a lot of the experimental issues under control.
- This project's strengths include its excellent chemistry, aims toward HSECoE data needs, and how it is helping the HSECoE's work toward Phase III.

Project weaknesses:

- The project has a strong flavor of trial-and-error at this stage; it is difficult to assess where breakthroughs to overcome barriers will emerge.
- The researchers must identify and deal with the impurities in a better way. They are going to have to deal with how much H_2 is released at room temperature. The project needs to provide more details on the new additive synthesis and catalysis. The project team needs to deal with regeneration issues and determine what the byproduct is on the release of H_2.
- Although the regeneration falls outside the scope of this particular project, it should be integrated in some way. A legitimate concern is that the IL may be incompatible with the regeneration effort. It would be nice to see the regeneration group(s) demonstrate compatibility with whichever IL is selected in FY 2012.
- There seems to be a distinct possibility that the limits to a dilution level to ensure a fully liquid system will result in missing the DOE weight and volume system targets.

- This project has no weaknesses.

Recommendations for additions/deletions to project scope:

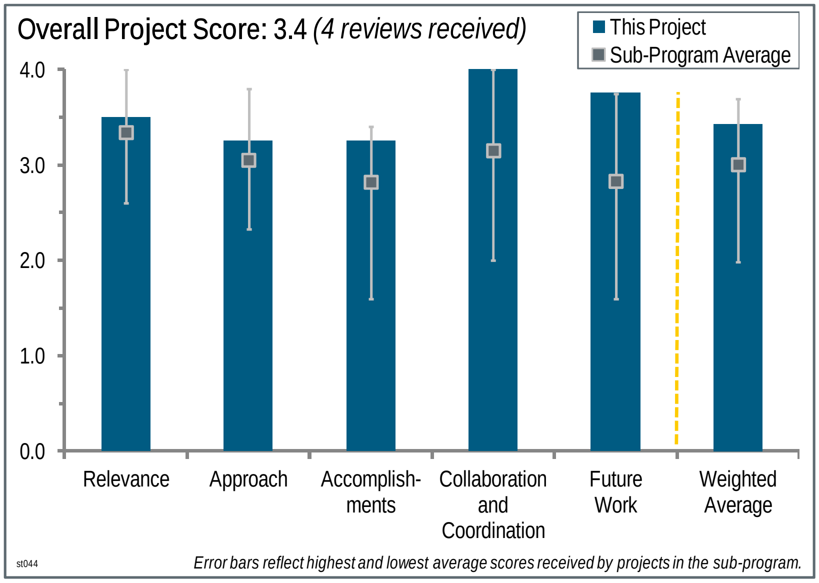
- The project team should not make any deletions.
- Successful storage materials, of course, require all performance criteria to be met. However, at this stage long-term stability tests are less important in this project than H_2 purity and maintaining suitable fluid characteristics over the required H_2 release range.
- Compatibility with regeneration efforts should be considered. It would be useful to collaborate with regeneration efforts elsewhere to determine the viability of this type of carrier. Stability measurements should be expanded—dehydrogenation should be investigated at higher temperatures. The project team should investigate how the liquid impacts kinetics (this may be done within the HSECoE). Impurities need to be better identified and ultimately reduced.
- The project team should accelerate interactions with the HSECoE and analysis groups to ensure that a practical and economic product will result from this work.
- This reviewer has no recommendations.

Project # ST-044: SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Metal Hydride and Adsorbent Systems

Ted Motyka; Savannah River National Laboratory

Brief Summary of Project:

The project's objectives for 2011–2013 are to: (1) develop innovative onboard system concepts for metal hydride and adsorption materials-based storage technologies; and (2) design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.5** for its relevance to DOE objectives.

- This project is highly relevant to DOE objectives and works toward DOE goals by providing good engineering input to the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- This project features development of innovative onboard system concepts for metal hydrides and adsorbents through systems modeling. The project eliminated metal hydride work and focused on adsorbent materials.
- This multifunctional project addresses virtually all aspects of the hydrogen (H_2) storage system in a comprehensive manner. As such, it generates and provides important information that is critical to the success of the DOE Hydrogen and Fuel Cells Program (the Program), and it fully supports DOE's research, development, and demonstration (RD&D) objectives and goals. With the decision to "divert" metal hydrides within the HSECoE, the presentation rightfully focused on one of the remaining leading candidate storage concepts—the cryo-adsorbent-based approach.
- The Savannah River National Laboratory (SRNL) project is an important component in the overall HSECoE technical effort. The project provides technical support to the HSECoE in the development of innovative system architectures and subsystem design concepts, as well as detailed modeling and validation of selected design concepts. The technical focus in 2011–2012 was on the development and validation of models for H_2 refueling and delivery in cryo-adsorbent systems. This effort directly supports the overall technical effort in the HSECoE and is relevant to the Program's RD&D objectives.

Question 2: Approach to performing the work

This project was rated **3.3** for its approach.

- The approach used in this project embraces an excellent balance of data assimilation, modeling, experimentation, and system validation. Each task is sharply focused on a critical barrier to meeting DOE's 2017 H_2 storage system targets. A clearer picture of what it will take for cryo-adsorption-type H_2 storage to evolve into a system that meets all DOE performance targets is emerging from this work. The 2013 DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) presentation for this project is worth looking forward to.
- The technical approach is focused on experimental and engineering modeling of flow-through cooling, design of cryo-adsorbent systems, and modeling of cryo-system performance with variations in media packing and operating conditions. Prior work included the system analyses required to make an objective go/no-go decision

on metal hydride system approaches. A logical approach that addresses the important technical barriers faced by cryo-adsorbent systems for onboard H_2 storage and delivery applications has been adopted in this project. Metal-organic framework-5 (MOF-5) has served as a prototype system in these studies. It will be important to continually assess the status of new material development to ensure that MOFs or other cryo-adsorbers with improved storage/delivery characteristics can be implemented in a straightforward fashion.
- The technical barriers are carefully addressed in a systemic manner, especially system weight, volume, efficiency, and qualitative cost. The overall engineering approaches are sound. The electrical heating/flow-through cooling concept, testing, and analysis are interesting. The current work is almost exclusively on cryo-adsorbent systems. Although discussed briefly in the HSECoE overview, more on why reversible hydride activities have been abandoned would have been interesting from this project's perspective.
- This project involves a significant amount of work testing models against experimental data. The researchers made adjustments to the models to better fit the experimental data. It is assumed that the project team performed a sensitivity analysis to convince the modelers that they were changing the right parameters for the right reasons. If the "experimental error" in the experimental data was determined, some elaboration would have been helpful. Perhaps it is possible that the earlier models are fine, and that parameters were adjusted to meet an experimental outlier. The research team had an excellent idea to test a series of gases, specifically nitrogen (N_2), H_2, and helium (He). It would be good to know if the model predicts different outcomes for the different gases and, if so, whether the model, adjusted for H_2, can fit the observables for N_2 or He. If this is the case, it would be a great way to test the model. If not, then it is unclear what can be learned from measuring gases besides H_2.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.3** for its accomplishments and progress.

- Excellent progress has been made toward identifying and, to some extent, resolving issues that control or limit the performance of cryo-adsorbent-type H_2 storage systems. Slide 6 of the presentation at the 2012 AMR nicely summarizes how this comes together for cryo-adsorbent refueling and desorption. Slide 12 of the presentation contains an informative summary of modeling results for several alternative cryo-adsorbent approaches that includes a snapshot of where things appear to stand with respect to meeting DOE H_2 storage system performance targets. The nature and number of new experimental and modeling results revealed in the presentation gave evidence that a significant amount of productive effort was expended on this project over the past year.
- An impressive amount of work has been conducted in 2011–2012 on engineering modeling of the cryo-adsorbent systems, particularly on the flow-through analyses, dependence of system performance on variations in operating conditions and material characteristics, and improved H_2 refueling and delivery schemes. It would have been helpful to provide more detail concerning the assumptions that are included in the model, as well as a straightforward analysis of model "sensitivity" to the key parameters. Without that information, it is difficult to assess the validity of the models or be confident about their predictive capability in an operational environment.
- The results are technically excellent and do much to define the basic challenges in achieving a cryo-adsorbent system that will meet DOE targets. The MOF compaction work seemed to be very useful. The results seem to be trending toward really low temperatures (e.g., 40 K), further adding to concerns about the general operational practicalities of cryogenic storage. The biggest gap between reality and DOE targets seems to be the loss of usable H_2 (dormancy). This problem was discussed by the principal investigator (PI) in the question and answer session. It was pointed out that this is a major component of the Jet Propulsion Laboratory effort.

Question 4: Collaboration and coordination with other institutions

This project was rated **4.0** for its collaboration and coordination.

- Strong collaborations are apparent for this project.
- Extensive and diverse collaborations, especially with numerous partners in the HSECoE, are ongoing, and those interactions are serving to significantly augment and leverage the SRNL project.
- The collaborations are excellent within the HSECoE. They are especially valuable with the University of Quebec Trois Rivieres (UQTR).
- Slides 4 and 21 of the presentation depict how this project fits into the larger HSECoE infrastructure. The project appears to be well coordinated with appropriate HSECoE partners, but only the National Renewable Energy

Laboratory, UQTR, Ford Motor Company, and Oregon State University are indicated as collaborators on the accomplishment slides. It would be interesting to know how all of the different modeling/simulation/validation studies mentioned from one partner presentation to the next actually fold together (one assumes they do).

Question 5: Proposed future work

This project was rated **3.8** for its proposed future work.

- The project team proposed several specific ideas that show thoughtful planning.
- The proposed future directions are very appropriate and will help complete the story.
- The future plans presented for this project do clearly build on past progress (particularly progress since the 2011 AMR) and are indeed sharply focused on mitigating barriers to meeting DOE's 2017 H_2 storage system targets. Surely some truly definitive findings will emerge from this project in the coming year with respect to cryo-adsorbent-based H_2 storage for fuel-cell-powered passenger vehicles.
- The future work is clearly stated and described in sufficient detail to allow reviewers to fully understand and appreciate the directions that will be taken in the future. The future plans represent a logical and compelling continuation of the present work and should provide useful information that will support the final system design. The decisions made by the PI and HSECoE management to conduct an objective evaluation of materials and down-select only a few promising candidates has allowed the project to focus more effectively on important technical barriers.

Project strengths:

- SRNL is doing a commendable job coordinating many partners and providing technical contributions.
- This project has an excellent engineering team and collaborations. This is an excellent example of what contributions to a Center of Excellence should look like.
- This project's strengths include having a comprehensive, well-structured research and development plan; appropriate expertise and experience; and a realistic approach to defining system requirements, addressing critical (progress-limiting) issues, and validating system performance.
- The SRNL team has a solid understanding of system needs and technical barriers that apply to the development of H_2 storage and delivery systems and subsystems. The PI and his colleagues have expertise and a strong background in all engineering aspects of the experimental and modeling efforts in the project. Extensive collaborations with other partners in the HSECoE provide useful support for the SRNL effort.

Project weaknesses:

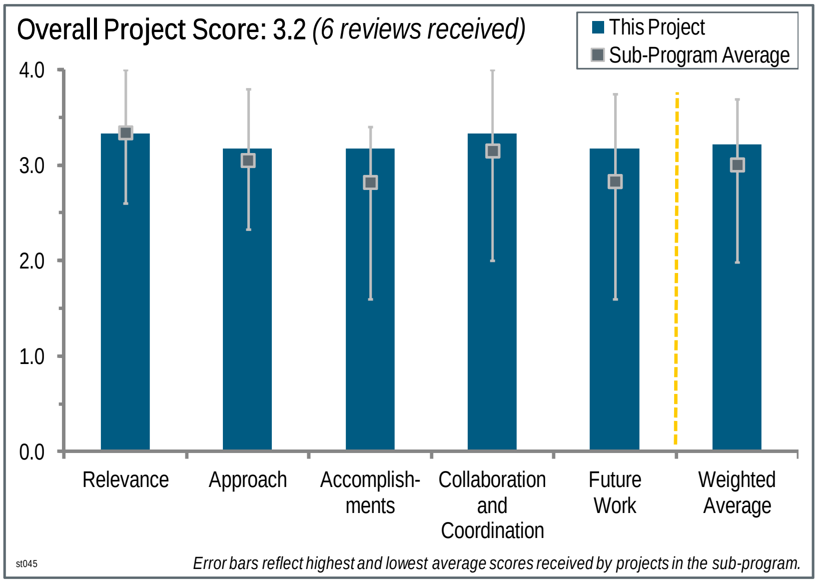
- The most significant problem is that no single material meets the DOE targets. Consequently, the SRNL team is forced to develop a system based on less-capable materials.
- It seems to be a bit of a stretch that the practical complexities and costs of cryogenic storage systems will be justifiable over relatively simple, ambient temperature compressed H_2 storage.
- This project has no apparent weaknesses.

Recommendations for additions/deletions to project scope:

- The project scope is well formulated. Not much can be done to improve it at this time.
- The project team should get some preliminary metrics on cost in the near future.
- A more detailed sensitivity analysis is needed in the modeling work in order to provide confidence in the accuracy and validity of the predictions derived from the model. It will be important for SRNL to be flexible with its engineering architecture and design efforts in order to be able to effectively incorporate improved materials that may emerge from other studies.

Project # ST-045: Key Technologies, Thermal Management, and Prototype Testing for Advanced Solid-State Hydrogen Storage Systems

Joseph Reiter; NASA Jet Propulsion Laboratory



Brief Summary of Project:

The objectives of this project are to: (1) identify state-of-the-art concepts and designs of hydrogen (H_2) storage systems; (2) discover and identify technical barriers to system development; (3) develop means and/or identify trajectories to overcome barriers; (4) describe and develop enabling technologies toward achieving targets; and (5) design, build, and test hardware components for model validation.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.3** for its relevance to DOE objectives.

- The ability to accomplish the objectives of this project is critical to a key candidate H_2 storage pathway for transportation.
- The project is addressing several technical aspects related to cryogenic storage that could support efforts to meet DOE goals and objectives.
- This project is relevant to the objectives of the Hydrogen Storage Engineering Center of Excellence (HSECoE). The Jet Propulsion Laboratory's (JPL's) work scope is consistent with the needs for designing a cryo-absorbent onboard storage system
- JPL has redirected part of its effort to address important cryo-system engineering issues. All aspects of the project (as it is currently framed) are well aligned with the DOE Hydrogen and Fuel Cells Program goals and fully support DOE research, development, and demonstration (RD&D) objectives.
- The JPL project is generally well aligned with the HSECoE goals and the DOE RD&D objectives. JPL has extensive experience and expertise in cryogenic system modeling, design, and testing for spacecraft applications. That experience is directly relevant to the present work on cryo-adsorbent systems for H_2 storage and delivery.
- The JPL role, developing cryo-pressure vessel technology, is very relevant to HSECoE efforts to develop a viable solid-state H_2 storage system. Because it appears that an ambient temperature system will not be an option going into Phase III, a low-temperature system will be required to enable a sorbent-based system that can be capable of meeting DOE onboard requirements.

Question 2: Approach to performing the work

This project was rated **3.2** for its approach.

- JPL's approach is to validate model results with coupon experiments and apply the model to the engineering design of system components. This is a sound approach toward achieving the objectives defined in Phase II. The approach lays the groundwork for Phase III prototype testing. JPL has the unique capability to perform burst-testing of Type I and Type IV pressure vessels at cryogenic temperatures.
- Each task is directed at one or more critical barriers to meeting H_2 storage system performance targets. The work done in the past year and proposed for the coming year on cryo-system design, modeling, and testing couples nicely with efforts at Lincoln Composites and Pacific Northwest National Laboratory. The emphasis on

insulation, outgassing, heat transfer, and durability is highly appropriate and much needed as prototype testing and concept validation become increasingly important aspects of the overall HSECoE program.
- JPL's focus has shifted to novel cryogenic technology development and implementation as the HSECoE has evolved and the reversible metal hydride development has been stopped. JPL is no longer the system architect for the cryo-sorbent system; that role has been assumed by Ford, which brings the perspective of an original equipment manufacturer end-user into clear focus. The remaining JPL tasks are well focused on resolving the issues of advancing thermal isolation designs, measuring outgassing from the pressure vessel, investigating downstream heat exchanger design, and pursuing cryo-burst testing of pressure vessels.
- There is a good and appropriate mix of modeling and experiments. One concern regarding the outgassing task of characterizing the impact is that it is a function of temperature, gas pressure, and the gas species. It is unclear if there is a way to understand the species' evolution as a function of temperature, life, and species partial pressure. The refocusing of the project and this investigator should aid in the timeliness and quality of the results at the end of the project.
- The approach is technically sound, but it could use some performance-related refinement, particularly in better understanding the product requirements for dormancy/venting. The objective of the cold composite pressure vessel burst is not clearly stated.
- The technical approach comprises work on cryogenic vessel insulation, vessel outgassing, design and testing of heat exchangers, and burst testing of cryo vessels. These tasks are important elements in the overall engineering effort on cryo-adsorbent systems in the HSECoE. The approach is logical and focuses on the technical barriers that confront the engineering development of an efficient cryo system. The de-scoping of the metal hydride effort in the HSECoE required a nimble transfer in technical direction by JPL. This was handled in a straightforward and timely way. The connection between an important aspect of the technical approach in 2010–2011 and the effort reviewed this year is confusing. In prior years, the principal investigator (PI) served as the "system architect" for the cryo-adsorbent system design process. In that role, he was responsible for coordinating engineering efforts across the HSECoE—an important and time-consuming task. However, beginning in 2011 it seems that role was assumed by D. Siegel (University of Michigan); in other words, the JPL PI no longer serves in that capacity. The presentation does not clarify that situation, and it does not discuss the revisions to the roles and responsibilities that accompanied that transition.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.2** for its accomplishments and progress.

- JPL appears to have taken a leadership position in the design, development, and testing of cryo-adsorbent-type H_2 storage systems. Testing and validation studies are providing critical design data and seminal insights concerning cryo-vessel performance. Some encouraging performance improvements were reported. Inconsistencies in outgassing results need to be ironed out. It would be interesting to know what gases are contributing to the pressure rise, and whether this effort relates to permeability studies being done by other HSECoE partners.
- Considerable progress was made in 2011–2012, especially in the area of downstream heat exchanger design and modeling. Important new results were also obtained on simulation and modeling of dormancy in a cryo subsystem. That understanding is critical to fully validating the system-level thermal performance in practical system operating conditions. Also, the development of a burst-testing chamber that was started in 2011–2012 will provide an excellent test facility for use in future HSECoE work.
- The heat gain reduction effort looks promising. It would be helpful to better understand what level of heat gain is acceptable—liquid natural gas storage products and characteristics could provide some guidance. Vibration tolerance, not just shock, needs to be evaluated for the Kevlar suspension system. In the downstream heat exchanger work, the extent of supplemental heating needs to be quantified.
- Despite the reduction in funding, progress since the last DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) has been good. The advanced Kevlar suspension system model has been validated and shows almost a 40% performance improvement over state-of-the-art systems. Outgassing experiments have been started, but the results have been somewhat inconsistent. More work is needed here to determine if outgassing will have long-term detrimental effects on the thermal isolation properties. Also, the species that are evolved need to be identified and a mitigation strategy needs to be developed. The cryo-burst facility design, which will

have the capability for 15,000 pounds per square inch burst of <20 L composite over wrapped pressure vessels at 77 K, has been completed.

- Modeling results showed a 38% reduction in parasitic loss for JPL's advanced thermal isolation design, which is welcoming news. However, for practical application, a three-dimensional dormancy is probably not acceptable to the consumers. JPL has developed a facility for cryogenic burst-testing of pressure vessels at 77 K and 40 K. Carbon fiber overwrap test vessels (6-L) have been manufactured by Lincoln Composites for burst testing at JPL's facility. JPL should consider extending the facility to collect fatigue data for carbon fiber composites (coupon size) at cryogenic temperatures.
- The project team has achieved a very nice design and build of the cryo vessel and the reduction of thermal conductivity using the Kevlar webbing. Visually (slide 9), concerning the loading and coupling of the suspension web between the tank and jacket, it looks like there may be an issue with a challenging vibration load with the somewhat complex structure. The dormancy general behavior is expected, but it is good to see some quantification from the model. While new tests are needed with the new system, the initial outgassing tests imply that there can be significant gas evolved if a vessel is allowed to reach the end of its dormancy period and reach close to the ambient temperature. Once cooled down again, the pressure will decrease, but with the increase of mass in the gas phase, the researchers should look at that effect. It would be interesting to know if there are any components of the composite overwrapped pressure vessel (COPV) that reach equilibrium partial pressures at the cryo temperatures.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The clearly identified collaborators are qualified and contributing.
- JPL has close interaction and collaboration with members of the HSECoE and frequent participation in Storage Systems Analysis Working Group meetings.
- While the partners were listed and there was mention and a slide referring to the collaborations, the degree was not clear in the presentation.
- Numerous collaborations and interactions with multiple partners across the HSECoE are effectively leveraging the impact of the JPL project. The coordination of this project with the "system architecture" effort (University of Michigan) could be defined in greater detail.
- The presenter provided a very clear picture of how the JPL project fits into the overall HSECoE program and outlined the specifics of the relevant connections with other HSECoE partners. DOE and HSECoE have developed a set of "specific, measurable, achievable, relevant, and timely" (SMART) milestones to "align" and "coordinate" technical work in Phase II. This should ensure a well-integrated effort throughout the HSECoE. Outgassing and permeability studies across the HSECoE should be carried out in a correlated manner.
- The collaborations with the other HSECoE partners are very good. The good communication between the team members developing sorbent-based systems has enabled good progress in this area. Additional collaboration with Lawrence Livermore National Laboratory (LLNL) is encouraged to take advantage of the knowledge gained with the cryo-compressed storage system.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- Future work is well defined for the three main tasks. The cryogenic burst-testing facility is a nice addition to the portfolio of the HSECoE.
- The future work is clearly identified and appropriate. More detail on schedule and decision points would be helpful.
- The presenter did an excellent job of laying out the future plans. The illustrations made it clear that JPL is ready to execute its plan. The modeling tools and test facilities are in place (or close to being in place). JPL has positioned itself as a key participant in the Phase III up-select process for the cryo-adsorbent concept.
- The future work represents a straightforward continuation of the 2011–2012 effort. Well-formulated milestones are in place, and the work addresses important technical barriers that remain in the development of an operational cryo subsystem tailored for onboard vehicle applications.

- The plans for future work look well thought out. The last task listed in the "Thermal Isolation" task could wind up being very important to the success of cryo pressure vessels in general. Scaled dormancy modeling and testing is also very important.
- The future work plans align well with the HSECoE objectives. However, there is some uncertainty regarding the role of JPL beyond 2012. If a cryo-sorption vessel is built in Phase III, it is unclear where it will be tested. There is also an opportunity for further collaboration with LLNL.

Project strengths:

- The project is generally well thought out, well executed, and covers important technical areas and barriers.
- The project has achieved overall solid progress on diverse activities.
- The project has a highly qualified team with extensive experience in a wide range of cryo system applications. All of the engineering efforts in this project directly support the overall goals of the HSECoE.
- JPL is focused on areas of its expertise. The team is well qualified and knowledgeable, and its capabilities for experimental validation appear to be very good.
- JPL has strong expertise in the area of thermal management modeling and testing. The new cryogenic burst testing facility and composite material outgassing facility are unique capabilities for DOE's Hydrogen Storage sub-program.
- Expertise and facilities are well suited to the barriers being addressed. The cryo-adsorbent system development effort across the HSECoE appears to be well organized and closely coordinated. JPL seems to be playing a key role. The JPL project presentation at the 2012 AMR was one of the best—clear, crisp, and concise.

Project weaknesses:

- Although much work has been devoted to improving the thermal insulation for cryogenic tanks, it does not appear that a viable solution to meeting DOE targets and consumer acceptance for dormancy is within reach.
- A minor issue is that it is not clear whether the engineering work on this project is sufficiently general to encompass new adsorbent materials that may emerge in future work.
- It is not clear if any consideration has been given to cost. It may not be part of JPL's scope, but some rough estimate should be considered to determine if a cryogenic system has any chance of being viable.
- The project team should assess potential COPV manufacturing and/or treatment approaches to mitigate outgassing effects.
- There are no apparent weaknesses in this project.

Recommendations for additions/deletions to project scope:

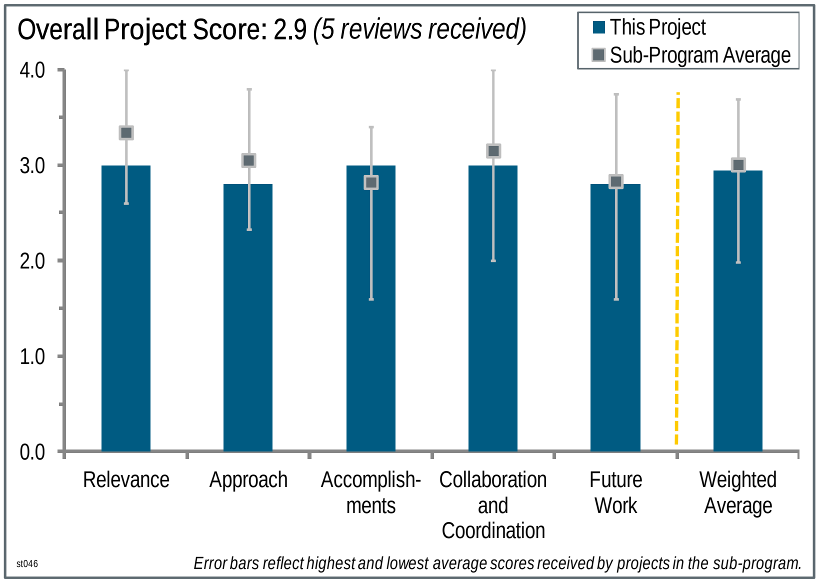
- Researchers should extend the cryogenic burst testing facility and procedure to allow the collection of fatigue data for T700 carbon fiber at 77 K and 40 K.
- The project scope looks fine as presently formulated.
- The project scope and level of effort seem fully consistent with the needs of the HSECoE. Clarification of the perceived change in the "system architect" role would be helpful.
- This project should expand its interactions with LLNL. Much of the development that has gone into the cryo-compressed system could benefit the HSECoE cryogenic systems work, particularly in the area of dormancy.
- The project team should pursue vibration and shock testing for cryo tank model validation. Unfortunately, this requires an additional tank to be built, or testing the current one prior to burst testing. The team should also get fatigue data on Kevlar in this webbing configuration. It would not be good if a thermally perfect cryo pressure vessel for cryo-adsorbents is created and performs well in static environments, but fails in shock, vibration, or fatigue environments. Perhaps the researchers can do an outgassing test with an inner chamber a few percent volume more than the sample and see if there is an equilibrium pressure as a function of temperature. Perhaps passivation of COPV is a possibility for a solution for outgassing. The project team should consider gettering as a purification method a little more. If there is a way to understand the outgassing overwrap component evolution as a function of temperature, service life, and species partial pressure, that could lead to new mitigation options.

Project # ST-046: Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage

Kevin Drost; Oregon State University

Brief Summary of Project:

The objective of this project is to use the enhanced heat and mass transfer that is available from arrayed microchannel processing technology to: (1) reduce the size and weight of storage systems, (2) improve the charging and discharging rates of storage systems, and (3) increase the performance of thermal balance-of-plant (BOP) components. This project addresses the barriers of reducing system size and weight, charging and discharging rates, and BOP.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.0** for its relevance to DOE objectives.

- The project has relevance if it improves performance.
- Maximizing heat transfer effects is critically important to sorption-based hydrogen (H_2) storage systems that operate at liquid nitrogen (LN_2) temperatures.
- This project deals with heat and mass transfer for H_2 storage within the DOE Hydrogen Storage Engineering Center of Excellence (HSECoE). The project is directed toward applying microchannel technology to reduce system size and weight, enhance charging and discharging rates, and reduce BOP complexity. The project is relevant to stated DOE H_2 storage goals and objectives.
- The major objective of this project is to use microchannel technology to enhance heat (and mass) transfer in a cryogenic adsorption H_2 storage system to permit rapid refueling of the media using LN_2 as the coolant. Using the microchannel approach, the additional weight and volume of the inserts is projected to be quite small (but not negligible, perhaps about 10%). This appears to address a relatively minor issue in the big picture of using off-board LN_2 for media cooling in the cryogenic adsorption option. A second objective is to design and test a microchannel combustor-recuperator-heat exchanger for H_2 during discharge. This would be a compact add-on to a conventional heat exchanger that would add only slightly to the weight and volume of the H_2 storage system. Although mass transfer enhancement was mentioned in the presentation, there was no specific example given.

Question 2: Approach to performing the work

This project was rated **2.8** for its approach.

- This project features a unique approach toward improving tank design.
- The project is sharply focused on the key issues. The stacked disc-microchannel approach is a good one. The use of aluminum rather than stainless steel is a key aspect.
- The project approach focuses on identifying and prioritizing opportunities for applying microchannel techniques. Novel concepts have been suggested for microchannel applications supported by subsystem prototype fabrication and testing for performance validation.
- The approach is to identify and prioritize opportunities for use of microchannel techniques in H_2 storage systems. Modeling, design, and testing for those opportunities is then conducted. The concept is to optimize the design and performance of a single unit cell, which would then be “numbered up” to the necessary full-scale

performance. One obvious question this approach raises is that of the effects of flow maldistribution among the multiple stages. This aspect was not adequately discussed. The system concept shows a 30-cm diameter "hockey puck." Because there was no discussion of the size needed for a full-scale system of 5.6 kg H_2 capacity, it appears that the full-scale system would also use 30-cm diameter sorbent pucks. This would likely lead to very high length-to-diameter ratios for the storage tank and potentially lead to high flow maldistributions.

- It is not clear whether this effort is fully integrated with the HSECoE. It would be good to see modeling efforts that show how much modular adsorption tank inserts (MATIs) improve fueling time for systems. The design seems to be unique to the hockey puck design, which may be too slow due to limited permeability. It would be good to know how it would work with the packed bed designs that the General Motors (GM) work suggests work well. Mass transfer limitations do not appear to be considered. The combustor is interesting, but earlier investigations have shown that catalysts deposited on microchannel walls are not durable enough for long-term applications. The investigators show their goals, but the baseline performance without the MATI is not clear, and it is not clear how much the MATI would improve the performance over the baseline system design.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.0** for its accomplishments and progress.

- The project has made significant improvements on the design since last year.
- Significant progress has been made on system designs and experimental verifications of system designs.
- Significant progress has been made in developing the MATI design concept for cooling and H_2 distribution. Performance and cost modeling have been accomplished based on volume manufacturing. Preliminary testing has been done on an adsorbent test bed in an effort to validate design concepts.
- The project has completed the initial feasibility study of the MATI and experimental validation of the oil heater design (it is not clear how this second item is related to the cryo-adsorption storage system concept). Process-based cost modeling is being conducted. The project is also exploring options for cost reductions. The significance of the results of the room temperature filling experiments is not readily evident. Laser welding of 316 stainless steel and 6061 aluminum plates has identified process issues that are being addressed. All of the components to be tested have been designed and fabricated.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- The project features an excellent set of collaborations that provide expertise from users of the technology.
- Extensive collaborations with HSECoE partners have benefitted this project substantially.
- This project is part of the HSECoE, which has multiple team members from industry, national laboratories, and universities.
- Although this is a different approach, collaborating with members (e.g., GM) working on heat management of the cryo-tank is recommended.
- It is not clear whether HSECoE modeling efforts are being applied to the MATI.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- The future work looks reasonable.
- The future plans basically involve a straightforward continuation of the various tasks currently underway.
- The proposed fiscal year 2012 and future work is consistent with the objectives of the project.
- Investigators say that the loss of physical integrity of the "hockey puck" will not be detrimental to system performance. It would be nice to see that assumption verified experimentally.
- It would have been helpful to see what the weight and volume of this tank system is (based on modeling optimization) compared to a standard baseline tank, in order to establish an apple-to-apple comparison, which would ultimately help down-select the best tank design. For the combustor recuperator work, it is highly recommended that this project consider other non-precious-metal catalysts in future designs.

Project strengths:

- This project has an excellent approach.
- The project features a strong, dedicated team and beneficial collaborations.
- A strength of this project is its novel concept.
- The experience in fabrication of microchannel devices is a strength of this project.
- The project has good collaboration and good modeling and model validation components. Another strength is the identification of important issues in the design and implementation of the project approach.

Project weaknesses:

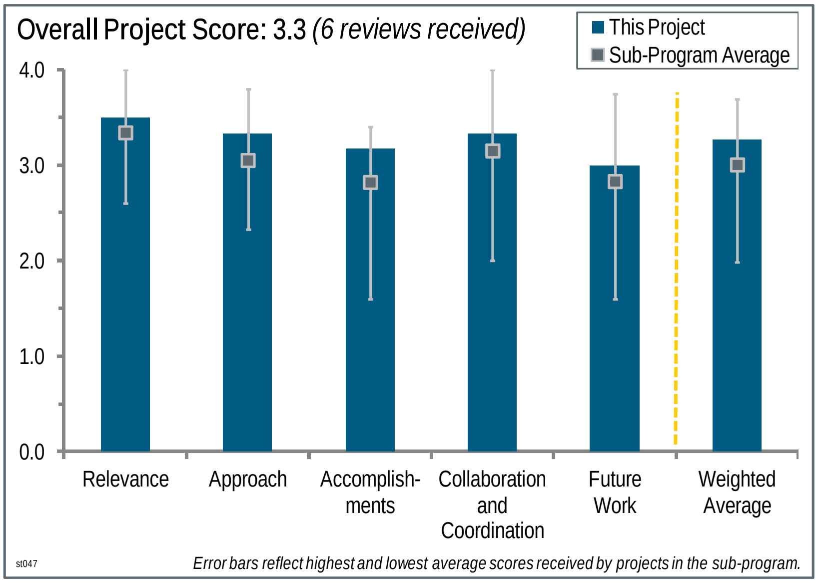
- The benefits of the MATI design are not as obviously quantitative as compared to others tank designs.
- As with other HSECoE projects, no attention is given to the forecourt implications of this technology.
- The joining of aluminum is a key aspect that may prove difficult.
- The proposed possible use of LN_2 means that there is a second cryogenic fluid onboard—this should be avoided if at all possible. Microchannel devices have been known to have fouling, plugging, and clogging problems under certain operational conditions. Likewise, catalyst delaminations in the channels in microchannel combustors and reactors have been a problem in some situations. Thorough prototype testing and validation of the candidate components and subsystems should be conducted as a part of this project. Compaction of the adsorption material in the "hockey puck" may damage conduction fins, if used.
- Manifolding and flow maldistribution in the multiple-stage MATI should be analyzed and addressed. The interface with the pressure vessel should be addressed because inserting the proposed assembly into a cryo-compressed H_2 storage vessel will likely not be a simple matter.

Recommendations for additions/deletions to project scope:

- The project team should establish the benefits of the MATI design quantitatively (using modeling optimization), as opposed to the test bed experimental approach.
- The researchers should consider long-term testing of the combustor to verify catalyst integrity.
- In addition to laser welding of aluminum, the project team might also consider looking into friction-stir welding. The team might want to look at aluminum cellular materials for increasing the conductivity of the hockey puck.

Project # ST-047: Development of Improved Composite Pressure Vessels for Hydrogen Storage

Norman Newhouse; Lincoln Composites



Brief Summary of Project:
The objectives of the project are to: (1) meet U.S. Department of Energy (DOE) 2017 hydrogen (H_2) storage goals for storage systems by identifying appropriate materials and design approaches for the composite container; (2) maintain durability, operability, and safety characteristics that meet the DOE 2017 targets; (3) work with Hydrogen Storage Engineering Center of Excellence (HSECoE) partners to identify pressure vessel characteristics and opportunities for performance improvement in support of system options selected by HSECoE partners; and (4) develop high-pressure tanks as required to contain components and materials of the selected H_2 storage system and operate the tanks safely and effectively in the defined pressure and temperature range.

Question 1: Relevance to overall DOE objectives

This project was rated **3.5** for its relevance to DOE objectives.

- The efforts in the project are important for a number of storage technologies.
- Lincoln Composites (LC) is developing Type IV vessels for materials-based systems and looking for vessel characteristics and opportunities for performance improvement and cost reduction. The work is relevant to DOE's goal of reducing the weight, volume, and cost of onboard H_2 storage systems.
- The tank work should be applicable to a wide variety of medium-pressure storage technologies.
- This project is very relevant to the HSECoE program. LC is investigating methods to reduce the costs of composite overwrapped pressure vessels, which will likely be the near-term solution for compressed H_2 storage on board vehicles. LC is also cognizant of the possibility of incorporating sorbent-based materials in the tanks and the possibility of operation at cryogenic temperatures.
- The outcomes of this project are progressing well toward the DOE objectives. This work appears more focused on utilizing existing technology and applying that science to the objective as opposed to creating novel technology. This lends this work to quicker commercialization, and therefore the work is in line with the objectives.
- This project is absolutely essential for meeting the DOE goals for an H_2 storage system for many well-established reasons. In the first place, pressurized H_2 gas (with or without adsorbent media) may end up being the best methodology when all Hydrogen Storage sub-program targets are considered collectively. Secondly, pressure vessels are likely to be required for sorbent-type systems, and possibly for metal hydride or chemical H_2 storage materials as well. Issues of cost, weight, durability, and safety are paramount for the pressure vessel. LC is clearly locked in on all of these issues.

Question 2: Approach to performing the work

This project was rated **3.3** for its approach.

- The work plan is designed to appropriately assess the major concerns associated with improving pressure vessel performance and cost.
- The principal investigators are taking a systematic approach to optimizing the cryo-tank.
- The project shows good integration between the collaborators, with each collaborator having a distinct and well-framed role. Consequently, the approach is logical and seems to follow a good flow with a focus on the objectives.
- Having established the baseline design in Phase I, LC is evaluating alternate designs and alternate materials (fiber, resin, liner, and boss) in Phase II to improve vessel performance and reduce cost.
- The approach that LC is taking in this project (i.e., slides 4–6) is well thought out, sharply focused on progress-limiting issues, and fully directed at exploring the best pathways to meeting H_2 storage system performance targets and costs. Norm Newhouse's presentation was excellent and left no doubt that the pressure vessel is presenting some daunting challenges that are being skillfully addressed. The research and development approach is based on consensus input from all HSECoE partners, as it should be.
- The approach by LC is well organized and is taking well-thought-out pathways for improvements in tank design and cost. The approach has been modified to investigate alternatives to Type IV tanks in response to comments from the 2011 DOE Hydrogen and Fuel Cells Program Annual Merit Review. The Phase I approach evaluated materials for cost and weight reduction as well as an increase in internal volume. Tank designs and materials were evaluated against operating requirements that were provided by the HSECoE team. The Phase II approach is to confirm operating conditions, select a baseline design and materials, evaluate alternatives, and fabricate bench-top test vessels. A common test vessel will be supplied to HSECoE partners to save time and cost for the project.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **3.2** for its accomplishments and progress.

- A large number of Type IV tanks have been fabricated and made available to the HSECoE.
- Given that in some instances LC's pressure vessels are only a part of a larger storage system, it is not simple to assess the company's direct contribution toward overcoming barriers. Nevertheless, LC is executing important technology assessment and validation work in support of the HSECoE.
- This project is meeting the necessary objectives and appears to be online for setting the stage for success in the subsequent phases. More effort, however, could be expended in looking further into the future to optimize the results beyond the current technology. Key accomplishments include resin characterization, even at cryogenic temperatures, and the manufacture of pressure vessels.
- The project team fabricated 21 six-liter test vessels (200-bar operating pressure)—three were used for burst tests, three were used for testing at cryogenic temperatures and leak tests, and 15 were made available to the HSECoE. Phase II test vessels were improved from Phase I baseline designs: 11% lower weight, 4% larger volume, and 10% lower cost. A significant portion of the improvement was attributed to reducing the carbon safety factor to 2.0 from 2.25.
- The lower safety factor, however, is not consistent with current guidelines established in SAE documents. The team also improved the winding technique to reduce peak stress near the boss opening, and cold-tested two vessels at 108 K and 205 bar for two cycles each. The number of cycles needs to be significantly higher to characterize fatigue behavior.
- Excellent progress has been made in the past year. The design basis vessel is well conceived, the level of analysis presented at the review was impressive, and the opportunity to actually hold on to a Type IV test vessel gave genuine encouragement that the project is moving forward into real systems. In addition to having made a sizable number of Type IV vessels for testing within the HSECoE, good progress appears to have been made in the area of materials development for the vessel. Modest improvements in terms of system weight, available storage volume, and cost were also reported.
- Accomplishments have been good in 2011. The test vessel criteria have been established based on consensus input from HSECoE partners. A baseline test vessel design has been established and 21 test vessels have been

fabricated. To address the reviewer comments from 2011, alternative all-metal and metal-lined composite designs were also prepared. Characterization of the behavior of the tanks at cryogenic temperatures is also planned. Preliminary results were shared for cold vessel testing that showed no effect on room-temperature burst properties. Preliminary designs for tanks that contain sorbents have also been considered.

Question 4: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The project features close collaborations and interactions with the other members of the HSECoE.
- There is good collaboration between the HSECoE and LC.
- This effort is supporting several other HSECoE projects, and the collaborations appear to be well coordinated.
- All parties seem to understand their role and have their roles defined well enough that there is little overlap, resulting in an efficient project.
- The HSECoE is doing an excellent job of ensuring that projects such as this one are well coordinated and integrated with the other partnering institutions. Frequent communications within the HSECoE partnership and timely meetings with the Tech Team are ensuring that design-related input is being transmitted in an effective manner.
- LC has established good collaborations with other team members to establish design criteria for test vessels and to consider alternative tank designs and materials going forward into Phase III.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future work is well planned. The project team should conduct more cycling tests and quantify the effect of the thermal expansion coefficient mismatch between different materials.
- The future work is reasonable and well defined. Further detail regarding schedule and success metrics would be helpful.
- The future plans do indeed build on past progress and will remain sharply focused on barriers. This project is orchestrated so that transitions from Phase I to Phase II and subsequently onto Phase III should occur seamlessly. It looks like LC has built enough flexibility into its approach to accommodate a reasonable range of design revisions based on future input from the other partners in the HSECoE.
- The future work plans are logical and flow from the results of previous activities. Efforts will focus on further design trade-offs and the closure of ongoing efforts in vessel characterization, alternative materials evaluations, and vessel designs.
- The future work looks to overcome a couple of key obstacles, such as optimization of the liner, validating the pressure vessels at cryogenic temperatures, and the ability to insert key components into the liner. These are excellent and necessary tasks to complete. However, resources could be spent looking at what the future H_2 storage equipment could look like in a novel approach instead of conforming and improving current technology to fit the DOE goals.

Project strengths:

- This project features a strong team.
- LC has substantial experience in developing and manufacturing Type IV tanks.
- The program is well thought out and addresses several important aspects of pressure vessel design and improvement.
- LC has the right experience, expertise, and resources to conduct this project in an effective manner. The tight collaboration structure within the HSECoE should ensure that the final pressure vessel design will be as close to optimum as possible.
- LC is a commercial supplier of Type IV tanks and composite materials and their experience should provide a realistic approach to cost estimation based on real-world practice. There were significant accomplishments in the past year. The work contributes to the efforts of other team members in materials-based systems and well as to

improving the picture for compressed storage. The funding for LC was increased substantially in 2012, enabling progress at a faster pace.
- This project is led by competent and experienced leaders and collaborators. This is especially true with the LC team; it is the right company to lead this effort. The team was able to manufacture the pressure vessels associated with the full storage system and complete cryogenic testing of the resin system. These are significant accomplishments pertaining to the ability of this project to reach commercialization.

Project weaknesses:

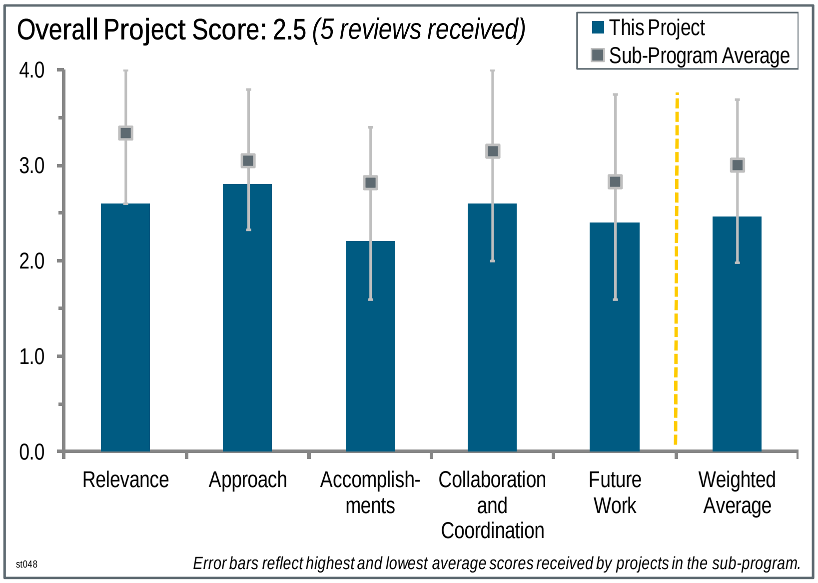
- This project has no apparent weaknesses.
- The amount of money expended toward this project appears to be a bit high in accordance with the accomplishments. Also, the efforts to optimize resin or fiber materials, or to characterize the desired properties of such materials, appear to be missing. With the volume potentials that this project and the other H_2 projects hold, material suppliers could be part of the collaboration to see if the ideal materials are possible.

Recommendations for additions/deletions to project scope:

- Investigators should involve polymer and resin manufacturers in work aimed at improving these materials.
- There is no need to change or modify any aspect of the scope of this project.
- LC should conduct pressure cycling tests for up to 1,500 cycles to meet SAE guidelines. The project team needs to quantify the effect of the coefficient of thermal expansion mismatch between different materials (fiber/resin, liner/fiber, boss/liner).
- Compatibility studies between vessel materials and storage materials that may be placed in the interior of the vessel are encouraged. There is the possibility for cooperation between the HSECoE and the Lawrence Livermore National Laboratory cryo-compressed team. If cryo-capable tanks are fabricated, a direct comparison of the capacity of a cryo-compressed system and the best available sorbent-based system could be made.
- New technologies are ever emerging in thermosets, thermoplastics, and fibers that could be an asset to this project. As a parallel effort within the collaborations established, time could be spent on identifying and determining the potential of new technologies. However, with such a good and practical start, the project should not get distracted by new technology and should continue its focus as currently developed.

Project # ST-048: Hydrogen Storage Materials for Fuel Cell Powered Vehicles

Andrew Goudy; Delaware State University



Brief Summary of Project:

The objectives of this project are to: (1) identify complex hydrides that have the potential to meet the U.S. Department of Energy's (DOE's) goals for hydrogen (H_2) storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions; (2) improve the sorption properties of systems that have been identified as good prospects for H_2 storage; (3) determine the cyclic stability of new materials and develop strategies for improving reversibility; (4) perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time; (5) extend the studies to include other complex hydrides that have greater H_2 storage potential; and (6) improve the rate at which the H_2 gas can be charged into a hydride-based H_2 storage tank, as well as improve the H_2 storage density.

Question 1: Relevance to overall DOE objectives

This project was rated **2.6** for its relevance to DOE objectives.

- The development of improved metal hydride systems that can meet the DOE targets is important.
- The project is largely relevant to DOE goals and targets, at least in terms of mass, volumes, and rates. Some targets are not much considered, such as H_2 impurities.
- Many of the reviewer comments made last year could be applied to this year's presentation. A number of the complex hydride systems that are being investigated are of very limited interest to the DOE Hydrogen and Fuel Cells Program (the Program) goals, given the high temperatures required for solid-state diffusion. Whether phase boundary or diffusion limited or something in between, a careful mechanistic evaluation would be in order. While some work has been performed on the lithium amide/magnesium hydride ($LiNH_2/MgH_2$) system that was suggested last year, with some apparent improvement to kinetics, the lack of detail in describing the reasons for kinetic improvement is problematic.
- This project addresses the behavior of a small group of complex metal hydrides or their mixtures (e.g., $Mg(BH_4)_2$-$Ca(BH_4)_2$, MgH_2-$LiBH_4$) with theoretical H_2 capacities that could meet DOE vehicle performance targets under ideal conditions. However, all of the systems evaluated during the life of this project have severe limitations due to poor kinetics, too low desorption pressures at practical temperatures (i.e., <473 K), or irreversibility after H_2 desorption. None of the systems is currently considered viable within the DOE Vehicles Technologies Program, although some might be appropriate for other early market fuel cell systems. However, there have been a number of published results by others in the international literature on essentially all of the materials being studied in this project.

Question 2: Approach to performing the work

This project was rated **2.8** for its approach.

- Many of the proposed reactions are well studied and not new. It was not clear if the principal investigator (PI) is aware of the considerable literature on previous work.

- The constant pressure ratio thermodynamic driving force approach is good for doing comparisons of different metal hydride materials. The research should concentrate on the most promising advanced metal hydride system identified to date and analyze it in more detail, particularly with regard to the understanding and optimization of additives on the metal hydride capacity and kinetics. Modeling of reaction pathways has been incorporated.
- The presentation of spectroscopic data, including X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and other techniques that might identify product phases, should have been included. With such a limited set of data presented, essentially showing only high-temperature dehydrogenation results with little indication of possible cyclability, the value of these systems, even as high-temperature reversible systems, is unclear. Part of the task 1 approach is to use XRD for phase identification. In the absence of knowing reaction products, there is no way of knowing the value of the systems that have been studied.
- Reactions (nearly always desorptions) of chosen hydrides were monitored by conventional volumetric/gravimetric methods either during heating ramps or isotherms. An emphasis was to produce kinetic data at a fixed free energy (i.e., constant pressure ratios) to extract time constants and presumably parameters such as activation energies, although none were obvious in the presentation. Only limited phase identification or characterization was apparently attempted (mainly via powder XRD), although some solid-state NMR was alluded to in the DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) presentation package, resulting in little insight into reaction pathways. Due to the properties of the selected hydrides, nearly all reported experiments were done at temperatures around 673 K, which is much too high for vehicle applications, and extrapolations were not made to more practical temperature regions. This is a definite limitation of scope for the project.
- The project looks at some relatively classic systems, both neat hydrides and destabilized mixtures. The data supports other DOE-funded projects. The very important property of kinetics is studied in detail and in a correct manner, scientifically—using constant pressures (absorption) and backpressures (desorption), as well as maintaining near isothermality. This careful technique is appreciated. Fundamental mechanistic studies, important for the whole picture, are still weak. Although such classic hydrides have been judged by the DOE Hydrogen Storage Engineering Center of Excellence as being unlikely to meet DOE system targets, continued work on them in this project is wise. It will contribute to the better understanding of hydrides in general.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.2** for its accomplishments and progress.

- A significant quantity of experimental results has been obtained. The comparisons of different catalysts are interesting.
- Much data has been generated. It is not only interesting, but it is also of potential practical value. The new catalytic results seem especially valuable. More mechanistic interpretations should have been developed beyond simple diffusion versus phase change limited rate control. For example, the NMR collaboration with the Jet Propulsion Laboratory should have been used to better help determine reaction pathways.
- It is interesting to try and understand the rate-limiting mechanisms of kinetics. However, the approach is somewhat simplistic—fitting data to diffusion controlled versus interface controlled mechanisms. There is a question about nucleation and various growth models (e.g., Johnson-Mehl-Avrami using different shapes of the nuclei). If the reaction is diffusion controlled, it would be interesting to know if it is possible to measure the diffusing species. This would be very important. Also, measurements of the activation energies for the various reactions would be extremely useful to the field.
- The presentation of work on MgH_2 provides no insights or data of value over the extensive quantity of literature published previously. The borohydride work shows improvement to desorption behavior, but as noted last year, no mechanism has been identified to indicate why a lower temperature desorption has taken place. An indication of the expected reaction pathway in the absence of presenting diffraction or NMR results of the product phase is necessary. Residual gas analysis of the desorbed gas phase would be important (e.g., NH_3 or B_2H_6). An indication of the desorption conditions, which can alter the kinetics of phase formation, is also critical. Desorption into vacuum can result in different phase formation than desorption into several bar of H_2 pressure. B_2H_6 formation would result in $B_{12}H_{14}$ formation that would essentially be irreversible. An analysis probing for the presence of all of these phases is necessary.
- Although the results reported in the experiments for the studied hydrides are probably reliable with respect to behavior under the test conditions, there is insufficient information on the decomposition products or

intermediate phases to allow detailed reaction pathways to be formulated and compared to theoretical analyses. While NbF_5 might be the most effective additive in decreasing the H_2 desorption temperature for the $LiBH_4/MgH_2$, and KH improves the kinetics for some $LiNH_2/MgH_2$ mixtures and not others, there is little insight being given into the actual microscopic processes. The project should do more in depth assessments of the actual changes in phase compositions and develop the underlying mechanisms if these systems are to be models for developing improved hydrides for storage applications. Evidence for extended cycling (i.e., hundreds of absorption/desorption reactions) of any hydrides in this project, which is needed for practical applications, was not apparent.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.6** for its collaboration and coordination.

- The researcher is collaborating with theorists.
- The collaborations are very good, but the results of these collaborations are not clearly shown here.
- While Johnson and Sholl are listed as collaborators, the list of destabilization reactions (which should also include the reaction enthalpies) was published by them. It was unclear whether these reactions were simply gleaned from the literature or if active discussions were involved. It was also unclear where the results are of the collaboration with the Caltech Solid State NMR Facility.
- The PI has explicitly interacted with at least a couple of theoreticians to select promising candidates for his experimental work, but it seems the PI has not contacted those researchers at the University of California, Los Angeles; Northwestern University; the University of California, Santa Barbara; and the University of Missouri-St. Louis who have been intensively doing first-principles modeling of defects and diffusion mechanisms for complex hydrides, including some that are being measured at Delaware State University. Although he has not previously explored collaborations to characterize samples from his experiments, the PI reported recent solid-state NMR studies, though none were included during the presentations. It would be interesting to see how these observations compare to the reactions given at this AMR. Some collaboration on applications of metal hydrides is occurring with researchers at the University of Delaware.

Question 5: Proposed future work

This project was rated **2.4** for its proposed future work.

- The proposed future work is good and should continue as planned. The project team should emphasize the development of more fundamental understanding via existing and new collaborations.
- The proposed future work seems to be a continuation of what is currently being done. There should be more focus on the most promising materials.
- The $MgH_2/LiBH_4$ system has been studied already. While the continuation of cycling studies is listed, it is not clear that this work has been initiated on the basis of the presentation. Unfortunately, there is nothing in the list of proposed work that suggests any more insights that are of relevance to the Program are to be gained from the planned work.
- There are some questions about whether any of the candidates being considered for future assessments are really viable for H_2 storage for vehicle applications. However, the project team should receive credit for supplementing the existing volumetric measurements of thermodynamics and kinetics characterizations with NMR and perhaps neutron scattering where deuterides should be used to maximize information content. Side reactions involving the formation of excessively stable phases have plagued borohydrides and amides.

Project strengths:

- The PI has extensive expertise and equipment to perform studies on the thermodynamics and kinetics of H_2 reactions with metal hydrides. He has developed systematic approaches to conduct these experiments.
- The project's sound experimental work is an area of strength.
- The project features good kinetic studies that are done properly.

Project weaknesses:

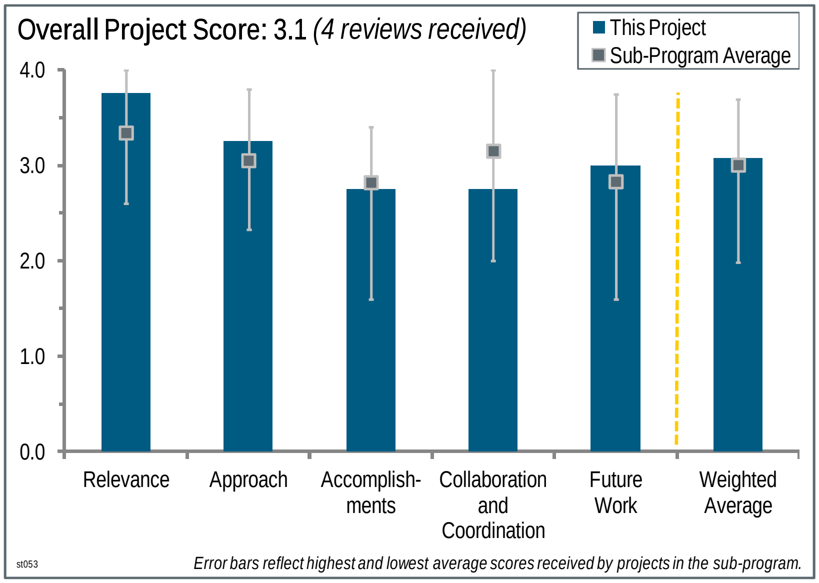
- The investigators need to better understand the details of the mechanisms that are going on.
- The project is still lacking important mechanistic connections.
- Much of this work has already been published or highlighted in previous Program reviews by other groups and the DOE Metal Hydride Center of Excellence. It is not clear whether deeper insights are to be gained by continuing to pursue this work if the level of effort expended is reflected by this presentation.
- Less-than-ideal complex hydrides and mixtures have been previously selected for study. In particular, those having significant reaction rates at temperatures above approximately 600 K will not meet DOE performance targets. Using only XRD to characterize reaction products is clearly insufficient for borohydrides, amides, and their mixtures.

Recommendations for additions/deletions to project scope:

- The project team should focus the project on the most promising system. Work on systems that require the higher temperatures for absorption/desorption should be dropped.
- The only recommendation is that the researchers should increase collaborations in order to expand the scientific and practical value of the nice kinetic and catalyst results.
- The PI should carefully review the most current hydride research literature to identify a system that would serve as a strong candidate to support both theoretical modeling of reaction pathways and have the potential to be a practical H_2 storage medium. The PI should not consider a system such as $LiBH_4/MgH_2$ or $LiNH_2/MgH_2$ that has already been widely studied, unless he can provide new insights into the fundamental processes. Finally, the PI should take full advantage of NMR and neutron scattering techniques to evaluate the phase compositions of his as-prepared and reacted samples.

Project # ST-053: Lifecycle Verification of Polymeric Storage Liners

Barton Smith; Oak Ridge National Laboratory



Brief Summary of Project:

The objectives of this project are to address operational cycle life issues, meet or exceed applicable permeation and leakage standards, and prevent the loss of usable hydrogen (H_2) in H_2 storage systems. Temperature cycling-permeation measurement tests are conducted on tank liners, including tests on new liner materials and post-cycling analysis, and test methods are developed for cyclic testing of sectioned storage tanks in collaboration with manufacturers.

Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.8** for its relevance to DOE objectives.

- The durability and permeation of liners is important, though not so much in question now. Understanding the mechanisms could be helpful.
- The H_2 permeability through polymer liners for H_2 tanks is a key issue related to tank safety and lifetime.
- The scope of the project is relevant to the goal set to test the durability of polymer liners. This is a key element in being able to establish standardized test methods and data for future companies involved in providing H_2 storage equipment. With the difficulty associated with safely storing H_2 and the large number of companies that will enter the field, test standards and methods are critical to ensure safe equipment.
- It is clear that the separate activities as reported are very relevant to DOE objectives. However, for someone not intimately familiar with the effort, there is some confusion. The effort to understand effects by separating elements (liner by itself) is important, but it took reading the questions and answers (Q&A) after the presentation to realize that only in future testing is it proposed to look at the liner behavior with the composite shell attached. It is unclear if additional support from the shell could change the results. In the Q&A period it was pointed out that H_2 absorption within the liner could cause volumetric expansion, and this could pose a delamination concern. Delamination is a real issue, and when it occurs, pockets form between the liner and the shell. The pockets would readily accumulate H_2. This sounds important, but it is not addressed. It would be helpful to present the "broad" picture or plan showing the relationship of information gained in this effort and information sought in terms of meeting the overall goals. It would be nice to see a presentation of the research goals addressed by this effort within the context of a good, high-level description of all of the issues and information people would like to know about how liners function in the composite overwrapped pressure vessel system. The technical target for operational life is identified as 1,500 cycles. This research effort has addressed the number of cycles as a DOE-specified target, but this does not seem sufficient by comparison to natural gas vehicle standards.

Question 2: Approach to performing the work

This project was rated **3.3** for its approach.

- The project features excellent facilities for H_2 permeability testing at high H_2 pressures.
- The cycling work is perhaps a little slow in coming; this is not largely considered a problem now. However, the new section testing could be very important.

- The team has put together a very good approach to creating a standardized and repeatable test method. However, testing is already ongoing in the industry by Type IV cylinder manufacturers, and there is no evidence that previous work was considered or used to help advance the project quicker.
- The approach makes good sense, but there is not enough description on the number of samples and how data from one manufacturer's liner is compared to another. It is understood that the information should not lead to revealing the manufacturers, but the presentation does not sufficiently distinguish results. The presentation could take more time to describe experimental apparatus and procedure.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- Progress appears reasonable for efforts undertaken toward DOE goals.
- Test specimens machined from actual polymer tank liners have been evaluated, which is good because the behavior of real production material is being characterized.
- The test methods have shown to be adequate in measuring permeation and in conducting the cycle testing. The project meets the goals as presented.
- The measurements of permeation and extracting kinetic factors from these are nicely done. It is also nice to see the changes offset to some extent. However, the knowledge merely allows for better understanding of a problem that has already been fixed. It is nice to substantiate the manufacturers' learning, but it would have been more important a few years ago. The argon measurements will provide an interesting bit of knowledge that will separate the effect of H_2 from the effect of pressure cycling. That analysis should be done expeditiously—as soon as there is enough of a data range to estimate the effect. The use of larger discs is a good improvement. It will be good if they do test alternate liners or liners subjected to some specific insult.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.8** for its collaboration and coordination.

- The project features useful collaborations that are sufficient and worthwhile.
- It would be nice to have collaboration with a polymer chemist who has experience in the permeation of gases, particularly H_2, through polymers.
- The team members are strong. However, one comment from Q&A suggests participation by a chemist. This seems like a necessity.
- It was difficult to understand in both the oral and documented presentations the roles of the collaborating partners. It would seem that more collaboration would be necessary from existing companies doing polymer liner research and from testing standard organizations in order to establish and promote the work completed as the future standard and to not duplicate efforts. The slideshow does mention these organizations as collaborators, but it is not clear how or what roles were played.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The proposed future work looks reasonable.
- The plans are fine. It would be nice if some novel candidate that a maker of tanks was interested in was evaluated. The section testing would be a very nice addition to the capabilities. It would be nice to see a time frame for this.
- The proposed future work is aimed at expanding the testing to other materials. The scope of this project appears to be aimed at creating a test method and in establishing a standard. Testing of other materials is good to develop a database, but it is not as important as the work to make this research stand out as the future method and standard. The future work for increasing the speed of the test is very good.
- The proposed work described is important. There has been no mention of the study of effects likely present in the "real" world. This would include the differential effects of flow from rapid filling and the potential harms caused by the occasional impingement of a high-speed particulate (it is not supposed to be there, but it is likely it will

happen, perhaps as a contamination introduced by the dispensing system). Also, the effects of pump oils should be studied.

Project strengths:

- This project features excellent capabilities for high-pressure H_2 permeability testing.
- There is good focus on the study of the liner materials with regard to permeation that is separate from the rest of the vessel system.
- This project's strengths include its unique equipment, ability to determine the effects of the pre-exponential factor and the activation energy in determining the liner permeation rate, and the ability to separate pressure from chemical impact.
- Very good methodology is being used and the results show repeatable, meaningful data. This approach should be used as the future standard. The technology being employed by the project team is excellent.

Project weaknesses:

- The researchers are not moving fast enough to be as helpful as they could be or as needed.
- The project could benefit from additional polymer materials expertise.
- There appears to be a lack of drive to make this technology the industry standard. This work is good enough to do that and would save time for other projects and companies in being able to better screen and test liner materials.
- The study must include the liner behavior as incorporated into the vessel system. Effects of interest are the support from the composite shell and the effect of liner expansion/delamination on permeation. It is not clear if 1,500 cycles sufficiently defines vessel performance for lifetime service. The study should attempt to understand the how and why for progressive changes in the slope and pre-exponential factor.

Recommendations for additions/deletions to project scope:

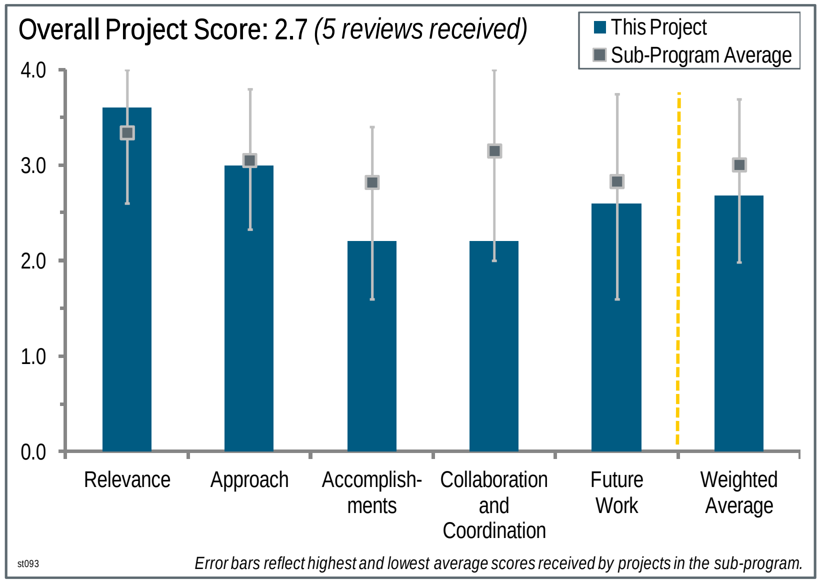
- The project team should set a time frame to collect the liner manufacturers and the standards organizations to promote this work and to advertise the ability to test multiple materials. A goal should be set to characterize a determined number of specimens and to make sure that each liner manufacturer understands and can access this technology.
- The project scope should include an increased number of cycles, effects of the shell, and effects of delamination. In addition, the project should include an investigation of the effects of likely contaminants, pump oils, and particulate.
- This reviewer could not identify any recommendations.

Project # ST-093: Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers

Felix Paulauskas; Oak Ridge National Laboratory

Brief Summary of Project:

The objective of this project is to reduce the manufacturing cost of high-strength carbon fibers (CFs) by means of: (1) significant reduction in the production cost of the polyacrylonitrile (PAN)-precursor via hot melt methodology, and (2) the application of advanced CF conversion technologies in development at Oak Ridge National Laboratory (ORNL) to down-selected formulations. The key technical issue is improving PAN melt stability by reducing the melt temperature below the degradation temperature.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.6** for its relevance to DOE objectives.

- The availability of low-cost and high-strength CF is critical to the success of the DOE Hydrogen and Fuel Cells Program.
- Developing cost-effective CF is critical for onboard hydrogen (H_2) storage, but this project is focused on producing precursor, not fiber.
- Decreasing the precursor costs by approximately 30% for CF is essential to substantially reducing compressed H_2 storage tank costs.
- This project is highly relevant to DOE’s objective of reducing the cost of onboard storage systems. Melt spinning also has the potential to reduce the manufacturing cost of CF and increase the production rate. Because precursors account for approximately 50% of CF cost and CF dominates the cost of the compressed gas storage systems, success in this project can bring down the onboard storage system cost.
- Melt spinning of the precursor holds much potential in achieving cost reductions for CF. This project is relevant in that it directly addresses the cost reduction goal with unique technology. However, the storage of H_2 is difficult and ultimately may require only high-performance CFs in excess of 700 kilo-pounds per square inch (ksi) tensile strength.

Question 2: Approach to performing the work

This project was rated **3.0** for its approach.

- The melt-processable PAN precursor provides an attractive path to achieve the goal.
- The approach focuses on modifying PAN to develop viable precursors for making CF using textile base processes. The key is the use of non-toxic solvents to form appropriate materials that form good fibers.
- The melt-spun approach has been partially proven by BASF in the 1980s and demonstrated in various U.S. patents and publications. The project seeks to improve PAN melt stability by reducing the melt temperature below the degradation temperature. In partnership with Virginia Tech (VT), ORNL is developing a new fiber spinning system with a multi-hole spinneret.
- This project aims to develop the precursor for the production of high-quality CF. The performance of CF depends not only on the properties of the precursor, but also on other procedures for production. The relation of

the properties of the precursor and those of the final products was not clearly shown by the principal investigator (PI).
- The basis of this project is keying on lessons learned from previous work that was completed but abandoned due to market conditions. This previous work provided an excellent baseline and established the direction of the project. The environmentally friendly elements of the project are key technologies and are fully integrated into the project plan.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.2** for its accomplishments and progress.

- The achievement of the team seems to be behind schedule.
- It is not clear why the project has only completed 20% of its work since the start of 2007. It is unclear if there was any risk mitigation plan during the execution of the project.
- The project seems to spend a substantial amount of time resolving issues from changes in precursor processing to form fibers. Hopefully, the lessons learned can be used to more quickly work through the issues and accelerate progress.
- This project appears to have made significant and lasting impact on the chemical barriers associated with melt spinning and has set the stage for further development. The filament quality is impressive. The area where progress is required, and is also being addressed, is in the handling and winding of the fibers. The chemical progress is impressive and the overall accomplishment would be rated as outstanding had it not been for the difficulties with the physical handling of the fibers.
- The project team has achieved good progress in producing the initial small count PAN precursor tows and demonstrating initial spinning with a hydrated melt of acrylonitrile/methyl acrylate ratio of 95:5. Physical properties and characteristics are approaching commodity-grade PAN precursor fibers. Some milestones were not met in fiscal year (FY) 2012 because of the unexpected challenge encountered with the winder system in the pressurized chamber. For several years, the PI has cited the 2007 Kline report that predicted an approximate 31% reduction in CF cost compared to the conventional wet-spun method. However, the Kline estimates were based on oil costing $60/barrel, which is about 40% lower than recent oil commodity prices. Additionally, the true gain cannot be quantified until the tensile strength and modulus of elasticity of melt-spun fibers are measured.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.2** for its collaboration and coordination.

- VT is the only external partner in this project. The project could benefit from collaboration and interaction with industry.
- This project has been conducted by a limited numbers of scientists. Collaboration with other people is recommended.
- If there is any coordination with partners outside of this project, the status of that coordination is unclear.
- It is not clear how much collaboration is occurring within the project.
- It is clear that the collaboration between VT and ORNL is highly functional and professional. The effort could have been improved had the partners looked earlier to experienced CF process engineers and/or consultants such as Izumi when they faced obstacles concerning fiber handling. Basic issues such as fiber winding and handling may be something with which the laboratory scientists are not fully experienced.

Question 5: Proposed future work

This project was rated **2.6** for its proposed future work.

- The efforts to continue improving formulations and fiber variability are good.
- The future work is well thought out. Emphasis should be placed on achieving good conversion of PAN filaments into CF because ultimately it is the quality of the CF, not the precursors, that matters.
- To continue the development of the precursor only is not favorable to realizing high-quality CF that is applicable to the high-pressure cylinder. It seems to be the time to extend the project to the fiber production.

- A risk mitigation plan is lacking from the future work. It is unclear if the CF strength will be measured after the conversion. If tensile strength does not meet the target, it would be nice to know what can be done to improve the performance.
- The future work discussed and presented focuses on the ability to make longer spools using proper filament winding. The FY 2013 “Future Work” is very vague and requires more detail and goals to continue the progress.

Project strengths:

- Fiber precursor cost reductions are essential.
- The PI is highly experienced in melt-spun precursor development. The project benefits from more than a decade of prior development in CF research and development at ORNL.
- Using an original idea, the precursor to high-quality CF has been developed. The enthusiasm of the PI is a strong driver of this project.
- The melt-processable PAN precursor approach is innovative and provides an attractive opportunity to significantly reduce the CF cost.
- The strengths of this project lie in the advancements made on the chemical capability to melt-spin the PAN precursor.

Project weaknesses:

- It is still early to project that the melt-spun CFs will achieve the target strengths (>600–700 ksi). Uncertainty in PAN conversion to CF could pose a serious risk to the success of this project.
- The relation between the performance of the CF and the property of the precursor is not clear. Thus, what appears to be an acceptable precursor may not necessarily result in high-quality CF.
- The project is moving slowly. A risk mitigation plan is lacking in the project execution phase.
- It was not clear from the presentation what other precursors and precursor processes may be used to reduce costs. It also seemed that a lot of effort was spent in an Edisonian way to resolve issues with small changes in formulation.
- The project’s weakness lies in what appears to be a manual melt spinning apparatus that would be well served to be automated to the point where the extrudate feeds directly into the melt spinning device and the winding and future post-treatment portion of the process.

Recommendations for additions/deletions to project scope:

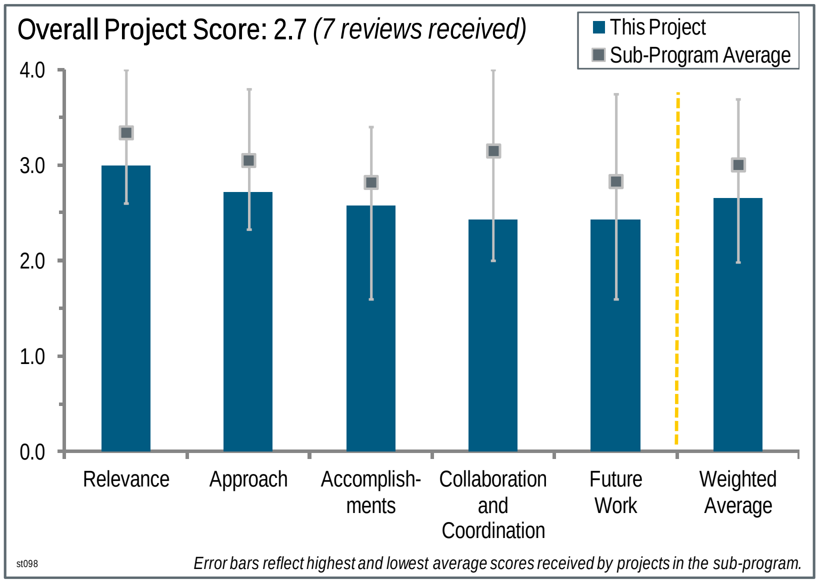
- Collaboration is very important for the next step of this project. It is recommended to collaborate with experts in CF processing.
- Perhaps a table of the different materials and processes that could be used and what their impact might be would be helpful to illustrate where the project should go and what could be achieved.
- To full understand the conversion capability of this precursor and to set the stage for further development, even to the point of commercialization, the goals of making continuous fiber of sufficient size and number should be added. These goals should be based on the CF line that will be used and contain multiple tow runs. Also, the cost data and goals should be recalculated and better understood, as this project should have more cost benefit than ST-099, which shows different numbers. Efforts should be taken to set goals and establish a plan for further scalability beyond just noting that consideration will be made.

Project # ST-098: Development of a Practical Hydrogen Storage System based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst

Craig Jensen; Hawaii Hydrogen Carriers, LLC

Brief Summary of Project:

The objectives of this project are to: (1) identify the liquid organic hydrogen carrier (LOHC)/pincer catalyst combination that gives the best combination of high cycling capacity and rapid dehydrogenation kinetics without LOHC degradation upon cycling; and (2) design a space-, mass-, and energy-efficient tank and reactor system to house the LOHC and facilitate hydrogen (H_2) release that can be easily interfaced with a fuel cell. The system needs to be able to store relevant amounts (6.6–8.8 wt.%) of H_2, be affordable and abundant, eliminate thermal management problems, and make use of existing and established infrastructure and materials.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.0** for its relevance to DOE objectives.

- The research is aligned with DOE Hydrogen and Fuel Cells Program objectives. While the liquids under study do not have a direct path toward gravimetric system targets, they do offer many advantages for an engineered system.
- The project is highly relevant to DOE objectives. The presentation notes a number of advantages of LOHCs; in many ways these materials can be seen as the ideal H_2 carrier.
- This project is well aligned with DOE objectives. An inexpensive LOHC with a homogeneous catalyst seems to be one of the more promising options for low-pressure automotive H_2 storage.
- The project seeks to obtain liquid carriers with adequate rates of H_2 delivery. Liquid systems have significant benefits for off-board regenerable materials. The project falls short of being able to meet DOE system gravimetric/volumetric targets. Low-pressure systems have benefits.
- The idea is to use organic liquid carriers, which is very close to Air Products' research and patents. The difference is the use of homogeneous catalysts rather than heterogeneous ones. It is not overly innovative. The overall idea is good, as organic liquids can exploit the current gasoline infrastructure. A serious concern is that the iridium (Ir) pincer catalysts are too expensive in terms of the metal and the ligands. There is a lack of further catalyst development using cheaper ligands and first-row transition metals, which are cheap. It is built on previously supported DOE work. There is an issue with weight percent if only a small amount of H_2 comes off. It is unclear if it will be enough to be useful. The use of a liquid will improve thermal management. Regeneration can be performed off-board.

Question 2: Approach to performing the work

This project was rated **2.7** for its approach.

- The key barriers are identified and there is a clear pathway to address them through chemistry and tank engineering. The development of the reactor in parallel with the chemical studies seems to be working well.

- Utilizing liquid carriers has been done and proven to have thermodynamic issues with H_2 release and discharge (apart from low H_2 content). Focusing on increasing the kinetics and reactor design for these carriers (which have already shown to have these issues) would not lead to carriers with properties approaching DOE targets.
- This work seems to build on the considerable amount of work done by a previous project headed at Air Products. It is not clear whether all of the work in that previous project and the knowledge gained are being most effectively leveraged.
- This project brings together two well-qualified, creative co-principal investigators (co-PIs) who have chemistry and engineering expertise to optimize the liquid H_2-carrier and reactor. There was some introduction about how modeling was being used to provide insight into catalysis design, but the description in the approach could have been more detailed. The results from each individual approach were communicated clearly and understood, but it was less obvious to see how the engineering was helping the chemistry and how the chemistry was helping the engineering. This is not to say it is not there, just that it needs to be communicated more clearly. The novel approach uses a homogeneous catalyst instead of a heterogeneous catalyst and looks to offer some advantages over heterogeneous catalysts, especially regarding the challenges with three-phase boundaries (gas/liquid/solid).
- The approach is built on demonstrated chemical principles and modeling methods to predict reactor performance. The plan and subtasks outlined in slides 12 and 13 represent a reasonable strategy for addressing the targets. The main drawback is that chemical factors for selecting new LOHCs (and perhaps catalysts) for study are not evident. The criteria in slide 9 give some background, but perhaps there are secondary chemical features in addition to hetero-substitution that can be identified and related to how well these criteria are likely to be met.
- The investigators have a good overall plan. They recognize issues beyond thermodynamics—for example, the constraints of melting points and boiling points. They need to consider and deal with the potential toxicity of reactants, intermediates, and products. They have an excellent connection to reactor designs with the General Motors (GM) partner. They need to optimize the catalyst and get away from Ir if possible because it is likely to be too expensive and potentially too rare. A survey of the amount of Ir available is needed. It would be nice to know what percent Ir catalyst is needed. The number quoted was that it cannot be more than 500 ppm. It is unclear what is currently being used. There is a lack of studies on catalyst properties such as the catalyst lifetime and turnover number (TON). There are close interactions with the GM reactor design team.
- The approach is generally reasonable, but incremental, compared to earlier DOE-funded work by Air Products (that was discontinued for lack of ultimate capacity), so the approach is lacking innovation.[Editor's note: The former Air Products' liquid carrier project funded through the Hydrogen Storage sub-program was not "discontinued" by the DOE but came to its contractual end.] If DOE targets are used as guidance, then the approach will not be able to meet the DOE gravimetric target for a system. The major difference is that the present research is focused on using more active low-temperature homogenous catalysts while Air Products focused on heterogeneous catalysts. The present approach does not address the disadvantages of having a catalyst in contact with spent fuel (reverse reaction limiting conversion). The approach did not address delivering H_2 at DOE target pressure, so the experimental approach of measuring kinetics and conversions at 1 atm seems unrealistic. The team should use 5 atm of H_2 backpressure as an experimental condition on which to perform these experiments on a reversible system, especially with spent fuel in contact with H_2 and a homogeneous catalyst. It seems the team has not thoroughly addressed the implications of the pressure regime for operation and the impact of these parameters on the absolute amount of H_2 that may be released. Ultimate capacity is limited to around 7 wt.% in the material (1 hydrogen atom per carbon or nitrogen atom); it is not likely to exceed this value and still have a regenerable system. The endothermic release of H_2 from the carrier must address heat inputs (and associated penalties, etc.). Higher-capacity compounds trend toward lower molecular weight, and thus higher volatility. Scrubbing of fuel and spent fuel from the H_2 stream were not addressed in the approach or in the future plans.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.6** for its accomplishments and progress.

- The project team designed the reactor and found improved kinetics using the pincer catalyst.
- The progress is hard to judge because this appears to have been an ongoing project that was not being funded by DOE. It is not clear how much progress was the result of DOE funding versus previous funding.
- This project has shown a few nice accomplishments over the past year. The kinetic studies are useful, but it looks like there has been limited progress getting H_2 off six-membered rings at reasonable temperatures.

- For such a short project, the amount of progress accomplished (the project is 40% complete) seems quite low.
- Many reactor designs were considered and many were eliminated, but it would have been useful to understand why specific designs were eliminated to appreciate the progress. Perhaps this insight would be helpful to the Hydrogen Storage Engineering Center of Excellence (HSECoE), specifically the chemical storage concepts being considered for endothermic alane. The presentation included a good description of the down-selection process to five-membered rings, but it would be useful to hear about plans for improving or maintaining catalyst stability. It is unclear if there is anything more to do beyond keeping the temperature lower, and how the different ligands affect stability. For example, a slide shows the TON for various ligands of about 250. It is unclear if there is a path forward to improve this TON for the Ir pincer catalysts, or if this TON is sufficient for the technical approach.
- There has been some progress; however, it appears the six- and nine-month milestones (slide 14) have not been met. The reactor design and modeling appear to be progressing according to plan. The dehydrogenation accomplishments presented also seem to be relatively small advances. For example, data presented on the system identified as most promising in the summary, methylperhydroindole, shows only the five-membered ring dehydrogenated at 160°C. This is a significantly lower temperature, but also a much lower H_2 content than the full dehydrogenation of decalin presented as background to the research. The PI gave the impression that further (proprietary) progress had been or is about to be made, but it is difficult to take this into account in a public review. It would be nice to see a more complete presentation of dehydrogenation that gives some measure of how facile the dehydrogenation is of the other parts of the molecules under investigation.
- The investigators have made good progress overall with some significant accomplishments, but there are critical issues that have not been addressed in terms of catalyst lifetime and TON, going beyond Ir and the current pincer ligands. It was nice to see the close connectivity with the GM reactor design team. This is a very positive part of the project. The reactor design work looks to be quite nice. It would be nice to know how much of the activation energy is just overcoming the endothermicity of the reaction. The researchers have very interesting work on five-member ring chemistry. They also remove the bridgehead hydrogen atom, which is an interesting scientific result. They have down-selected a set of compounds. There are no real details on the compounds they will use or their cost for first fill.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.4** for its collaboration and coordination.

- Their collaborations are satisfactory. Hawaii Hydrogen Carriers and GM work together effectively. The only external collaborator is Oregon State University.
- The collaborations seem somewhat limited. Collaborations with other groups interested in liquid carriers (e.g., Shih-Yuan Liu at the University of Oregon or Air Products) would be useful.
- Although the project seems to be a good fit within the HSECoE, no collaboration between the two seems to exist.
- Scott Jorgensen at GM and Craig Jensen at Hawaii Hydrogen Carriers work really well together; they are highly collaborative and synergistic.
- The collaboration between the co-PIs is good, but the level of collaboration was not so clear with the HSECoE, especially the chemical storage groups working on reactor designs. It would be interesting to know if any of the discarded reactor designs in this project are similar to the reactor designs considered by the HSECoE. It would be invaluable to share thoughts on what makes a good reactor for a liquid carrier, either exothermic ammonia borane or endothermic alane.
- There is some collaboration, perhaps even beyond the partners listed on slide 20, judging from the co-authors on the presentations listed. However, collaboration does not seem to be a strong feature of this project; for example, there are no accomplishments acknowledging assistance from outside institutions. It is likely that there are significant ties between the reactor work and the HSECoE in particular, and that some of the other participants in DOE H_2 storage research could make contributions. These relationships need to be developed and highlighted in future reviews.

Question 5: Proposed future work

This project was rated **2.4** for its proposed future work.

- It is highly recommended to focus on new carrier design.
- Proposed future work involves completing kinetic studies of perhydro-indolizidine dehydrogenation. It appeared that the studies were over a good temperature range. It was not clear what was needed to complete the studies. It is unclear if there are plans to measure the vapor pressure and volatility of the smaller five-membered ring organic liquid carriers. The reactor design could not be any more ambiguous: "Determine properties to meet different DOE targets."
- Much of the future work proposed is to conduct kinetic studies of various LOHCs. While this is important, the thermodynamic issues noted in slide 12 and discrimination between kinetic and thermodynamic limits should be addressed because many of the LOHCs presented have undergone incomplete dehydrogenation. The cycling studies proposed are a valuable component of the project, and it is sensible to conduct this for only the best-performing LOHC identified.
- The investigators have a good plan on where to go with what they have done. They need to look at new catalysts beyond Ir. They also need to do studies of catalyst lifetime and TON for the ones they do have. The proposed regeneration work is good. The proposed reactor work is good.
- Cycling studies will be critical to determine viability. In addition to determining the capacity retention during cycling, it will be important to determine how much catalyst is lost with cycling and how this will impact cost.
- It is hoped that the PIs will take the recommendations offered and improve their approach to address the potential for reaching equilibrium-limited (low) conversion when running against 5 bar of H_2 (delivery pressure to the fuel cell). However, even if the equilibrium limitations are removed, these materials cannot exceed around 7 wt.%, so it is exceedingly difficult to imagine how they can meet DOE targets, particularly the "ultimate" targets.

Project strengths:

- This project features a very capable staff.
- This project has a very capable team of co-PIs with extensive experience to carry out the required tasks.
- The project is well founded in good scientific principles, and the background literature has been researched and understood. The reactor design is being carried out using sound methodology with good links to commercial application.
- The researchers are making good progress on a good, but not original, idea. The use of a liquid fuel system makes it more likely that it can use some of the existing infrastructure. They have a potentially working system. There is a good effort with the GM reactor design team.
- This project is focused on one of the more promising options for automotive H_2 storage. The project seems to be making nice progress, especially with the development of the liquid organic carrier in parallel with the reactor.
- Strengths of this project include two really good PIs working together; a liquid carrier; low-pressure systems; and simple, well-understood chemistry and catalysis.

Project weaknesses:

- There seems to be a lack of coordination with HSECoE on the reactor design. One would assume there is much to be learned from each party.
- The project has looked only at incomplete dehydrogenation of LOHCs so far, and a pathway to increasing the realizable H_2 capacity while maintaining low-temperature release has not been articulated. Rehydrogenation has not been investigated. The project duration—less than two years—is relatively short to achieve difficult goals.
- The investigators will need to get all of the reactions near 100%. They need to go beyond Ir pincer ligands, and they need to address catalyst lifetime and TON as well as cost. The presentation was lacking details on the compounds to be used and their cost. The team needs to address toxicity issues with the proposed process; there may be none, but they should state that.
- H_2 release from the five-membered rings is 2–3 wt.%, and it is approximately 6 wt.% from the six-membered rings. Given these constraints, it seems likely that this work will fall short of the targets (but it will probably still be better than most of the other options). Catalyst cost is a weakness, and it is unclear if the low catalyst

concentrations needed to keep the cost down will be suitable. Use of a homogeneous catalyst may result in some catalyst loss during operation.

- Although the project seems to be a good fit within the HSECoE, no collaboration between the two seems to exist. Utilizing liquid carriers has been done and proven to have thermodynamic issues with H_2 release and discharge (apart from low H_2 content). Focusing on increasing the kinetics and reactor design for these carriers (which have already shown to have these issues within the project) would not lead to carrier properties approaching DOE targets.
- Regarding the homogeneous catalyst, the ligand is likely to be quite expensive. Keeping the homogeneous catalyst in contact with spent fuel in the presence of H_2 makes dealing with the back reaction a significant problem—there could be equilibrium limitations. The limited ultimate capacity of around 7 wt.% material makes it difficult to meet system targets, and there is no path forward to increase capacity. There exists only one hydrogen atom per carbon or nitrogen atom. This has the identical approach to the Air Products liquid carrier project that was discontinued by DOE, due to the lack of ultimate capacity. [Editor's note: The former Air Products' liquid carrier project funded through the Hydrogen Storage sub-program was not "discontinued" by the DOE but came to its contractual end.]

Recommendations for additions/deletions to project scope:

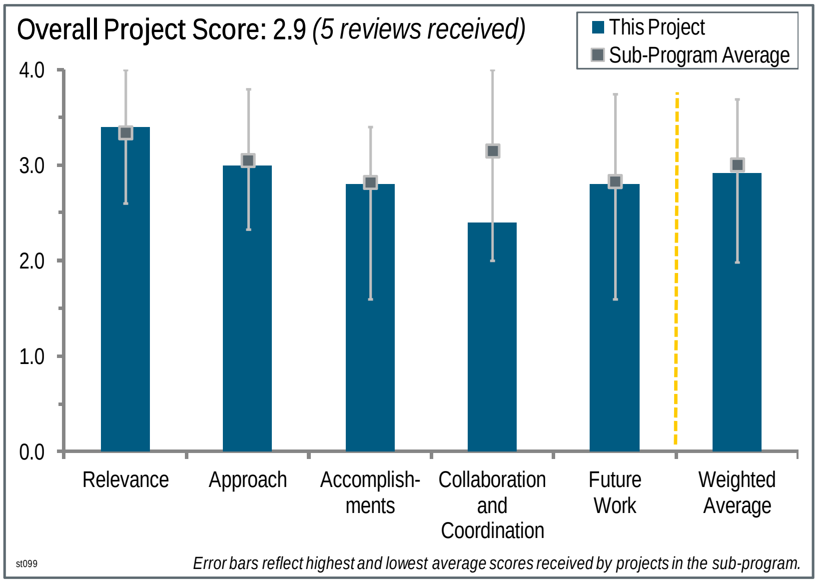
- It is unclear if using Arrhenius rate parameters revealed what temperature, catalyst concentration, and reactor length is required to achieve a release rate of 2 g H_2/second to provide the fuel cell under full load.
- The project team should address other types of catalysts and study catalyst properties.
- The future plans and project scope seem appropriate. It is highly recommended to focus on new carrier design with acceptable thermodynamics and high H_2 weight percent.
- If the project is continued, the team needs to perform kinetics for conversions at the delivery pressure that the DOE target specifies (5 bar for fuel cells to demonstrate that there are or are not equilibrium limitations on conversions, or rates of H_2 evolution).

Project # ST-099: Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)

Dave Warren; Oak Ridge National Laboratory

Brief Summary of Project:

The purpose of this project is to develop a textile-based precursor that uses polyacrylonitrile (PAN) produced in high-volume textile mills (carpet, knitting yarn, etc.), and to develop a reduced-cost high-strength carbon fiber (CF) based on textile spinning processes. High-strength CF enables durable, lightweight, compressed hydrogen (H_2) storage vessels to be manufactured. The project approach includes identifying candidate PAN-methyl acrylate (PAN-MA) resins, determining fiber spinning parameters, and determining the conversion protocol.



Question 1: Relevance to overall U.S. Department of Energy (DOE) objectives

This project was rated **3.4** for its relevance to DOE objectives.

- Developing cost-effective CF is critical.
- The development of lower-cost fibers is essential to low-cost H_2 storage systems.
- This project is relevant to DOE's objective of reducing the cost of CF for use in high-pressure H_2 storage tanks. Development of a low-cost commercial textile precursor provides a short-term, fast-track approach to achieving the objective.
- This project is extremely important to many of the DOE goals, both in automotive and non-automotive fuel cell technologies. From an automotive view, this may be the most important short-term work funded. From a non-automotive view, it is still important in advancing technology.
- This project is aimed at creating an identical CF to one that is already commercially available today. The goal of the project is based on creating cost savings through improved throughput of the precursor and the use of MA as a co-monomer. With little data available on the competition's relationship between throughput and cost, and MA only being around 5% of the polymer, this project lacks more detailed and specific goals other than the overall cost reduction based on a theoretical cost model. The availability of a lower-cost, air-gap-spun fiber would assist the overall DOE efforts concerning global precursor supply.

Question 2: Approach to performing the work

This project was rated **3.0** for its approach.

- The overall approach is sound—looking for appropriate fiber resins, spinning them, and determining the conversion protocols to make them CFs. Working with a potential supplier to the world is excellent. The materials chosen are good ones.
- The CF precursor is not produced in the United States, but by a partner in Portugal. To avoid risk, it is better to have the precursor producer in the United States. The "Underestimating of the difficulties of that task" section on the summary slide makes it seem as if there is an issue of planning with this project.
- This project is leveraging previous projects funded by the DOE Vehicle Technologies Program to deliver a fast-track approach to produce high-strength commercial textile precursor. FISIPE is responsible for producing the

precursors and Oak Ridge National Laboratory (ORNL) is responsible for developing the conversion protocol and fiber spinning parameters in order to achieve the highest fiber properties possible.
- Identifying ways of making fibers to decrease costs is extremely important. The use of standard textile manufacturing is a good approach. However, the use of a limited number of precursors and manufacturing techniques may not achieve all of the possible benefits.
- The principal investigator (PI), his team, and the primary collaboration partner have a very good technical approach to this project. They have sufficiently addressed many of the obstacles in modifying an acrylic fiber line into an air gap spinning line, and notable progress is being made. The key to the project will be the post-spun treatment (stretching, washing, drying, etc.) and the resulting operability of the CF during stabilization and carbonization. The improvement will need to be an increase in the target mechanical properties of the resulting CF to meet industry standard properties of 700 kilo-pounds per square inch (ksi) and 2.0% strain.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- The milestone of March 2012 has been completed, despite the delay with the equipment setup.
- The second trial exceeded the milestones with a variability of 2%–10%. It seems that little progress has been made, but in fact there was a lot of work required to get to where they are.
- There have been significant accomplishments made in creating the air-gap-spun technology. This represents a notable advancement over the technology employed by the collaborating partner. However, the real results will be the processing of the precursor in a larger-scale CF trial. However, the line retrofit did take longer than expected.
- This project has just completed its first full year. Progress was somewhat slow because of longer-than-expected time for FISIPE to retrofit its equipment to produce a PAN-MA precursor and a delay in setting up the polymerization and fiber spinning equipment at ORNL. Three precursors were down-selected for further development. One of the three precursors (F1921) was chosen for spinning trials. Results showed a large variation in tensile strength (282 to 419 ksi) and tensile modulus (27 to 36 million pounds per square inch [msi]). Goals are to reach 650 msi tensile strength and 33 msi modulus. If the goals in tensile strength and modulus are achieved, the commercial textile precursor has the potential to bring down the cost of CF substantially.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.4** for its collaboration and coordination.

- This project has few collaborators, but they are the right ones.
- ORNL partnered with FISIPE. There is no interaction or collaboration with others in the industry.
- The precursor is produced in Portugal and the carbonization is conducted at ORNL. It seems to be a good collaboration. However, it would be perfect if both organizations were in the United States.
- It was not clear how much collaboration was occurring and if the project was actively looking at the most state-of-the-art techniques that could be used to reduce costs.
- ORNL has been providing very effective and timely work to the collaborating partner, with whom ORNL states it has an excellent working relationship. The lack of cooperation appears to be concerning passing information from the collaborating partner, FISIPE, to ORNL, because the key elements that would help ORNL validate its effectiveness in meeting the cost target are not available, per the PI's comment that it is proprietary to FISIPE's business. More detailed conversion information concerning the plant and its operations parameters is necessary for ORNL to quantify that it is actually able to meet the cost targets.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- The plans are OK, but they are not overly ambitious.
- A lot of work needs to be done just to optimize with present manufacturing processes.

- Future plans are to improve precursor purity and spinning of rounder fibers, as well as optimize tension limits in stretching fiber. The team also plans on converting the other two down-selected formulations. The time constraint in this two-year project could compromise the planned activities.
- The gate is significantly high. Plans explaining how to reach the target of 550–750 ksi strength in April 2013, which is double to that of March 2012, should be shown in much more detail.
- The future work to convert the latest precursor into CF is the major effort going forward. However, the "Future Plans" slide does not address the post-spinning processes of stretching, washing, drying, and finish application, which are key contributors to meeting property goals, achieving stabilization efficiency, and eliminating "baby" filaments. It is unclear in the work whether or not ORNL will be an integral partner in this phase of the process, or how this part of the work will proceed.

Project strengths:

- The use of textile manufacturing techniques is a good approach.
- ORNL has many years of experience from previous projects in the development of low-cost CF.
- ORNL's collaboration with the Portuguese company seems to be a good idea, under the condition that no United States company can make the precursor of high-quality CF.
- Strengths of this project include its possible cost reduction and partners that are perfect to do this and move it to production.
- The strength of this project lies in the technical team that is assembled and the use of MA as a co-monomer. The overall goal of providing additional precursor capacity in the global market at a reduced cost is key to the CF industry as a whole.

Project weaknesses:

- There is no producer of precursor in the United States.
- Lack of speed is a weakness of this project.
- The project has passed its mid-point in terms of duration (for this two-year project), and there is still much to prove. One does not get the feeling that the schedule has room for delay or error, thus there is significant risk that the project will not achieve its goals on time and on budget.
- The project should be very active in identifying potential methods that could reduce costs and increase manufacturing rates. Also, the effort should at least look at what other precursors could provide and if cost reduction can be achieved through this route.
- This project is helping to fund the conversion of an acrylic fiber line into a line that produces PAN fibers for conversion into CFs. The weakness lies in the fact that this is not new technology, as this exact transformation has been completed by most of today's CF producers as long ago as the mid-1970s. The use of MA is a unique factor in this project and appears to be a key element in the cost reduction. However, the realized impact of using MA has yet to be fully characterized because impacts to conversion yield and fiber quality are key cost elements that do not appear to be fully quantified in the cost model.

Recommendations for additions/deletions to project scope:

- Combining or merging ST-093 and ST-099 should be considered.
- The project team should bring the polymer choices as far forward as possible in the process to maximize process development time on the polymer that will be used, not other polymers. The team should do what is needed to pick up the pace.
- A low-cost manufacturing roadmap should be developed to identify the baseline proposed and to identify other state-of-the-art manufacturing steps or processes that could be used to bring costs down even further.
- The addition of more detailed and incremental goals would assist in the down-selection of the precursors. Measurements and analysis surrounding the physical properties of the precursor and how those properties are affected by polymer dope filtration and all aspects of the PAN spinning process need to be developed to reduce the expense and time associated with running large-scale CF trials on the pilot lines associated with the collaborating partners. In addition, conversion rates and qualitative fiber parameter goals need to be established in order to understand whether or not the cost goal will be met.